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Exploring Vivianite in Freshwater Sediments – From the Detection of Mineral Grains Towards the Understanding of Their Occurrence

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So many of our dreams at
first seem impossible.
Then they seem improbable.
And then, when we summon the will,
they soon become inevitable.

Christopher Reeve

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Summary

In this thesis, the occurrence and environmental relevance of vivianite in freshwater sediments were explored. Vivianite, $Fe_3(PO_4)_2 \cdot 8\,H_2O$, is the most common reduced iron phosphate mineral which forms in sedimentary environments. Not much is known about the mechanisms which lead to vivianite formation in surface sediments, and about the quantitative role of vivianite in phosphorus sequestration. Oxidised iron compounds efficiently bind phosphate but these compounds are solubilized under anoxic conditions. Vivianite formation may significantly contribute to phosphorus retention in anoxic sediments, emphasizing the role iron plays in the long-term sequestration of phosphorus under reducing sedimentary conditions.

To render new insights possible, emphasis was put on the development of a sediment preparation method which allowed the direct identification of vivianite by powder X-ray diffraction. The identification of vivianite was achieved after application of a heavy-liquid separation of water-free sediment. Vivianite crystal aggregates, appearing as dark-blue nodules, were enriched in the high-density sediment fraction which was key to demonstrating the presence of the mineral. For the first time, vivianite was quantified in surface freshwater sediments, taking advantage of the paramagnetic nature of vivianite. The study examplifies that vivianite can significantly contribute to the phosphorus retention in surface freshwater sediments, accounting for 10-40 % of total sedimentary phosphorus.

The formation of vivianite crucially depends on the availability of dissolved Fe^{2+} in pore waters. Vivianite formation is favoured as long as the supply of dissolved Fe^{2+} exceeds the production of sulphides. In the present study, the sedimentary sulphur to iron ratio has been proposed to be a valuable indicator for the conditions that are important drivers behind the formation or absence of vivianite. Vivianite has been detected only at a molar sulphur to iron ratio smaller than 1.1. Theoretically, if the molar sulphur to iron ratio does not exceed a value of 1.5, vivianite formation is favoured because mineral formation is not restricted by the supply of Fe^{2+}. Notably, it has been demonstrated that eutrophication and the accompanied increase in sulphide

production hampers vivianite formation, leading to a decreased phosphorus binding capacity of sediments through increased sediment sulphidization. The present study also revealed, that an iron addition as a measure of lake restoration can trigger vivianite formation, and significantly increases the long-term phosphorus retention of sediments.

Discrepancies between pore water saturation calculations and the absence or presence of vivianite crystal aggregates in specific sediment depth layers demonstrated that supersaturated pore water is not sufficient to predict the occurrence of the mineral in situ. Pore water saturation calculations are usually based upon macroscopic measurements. However, mineral nucleation and crystal growth take place on a nano- to micrometre scale, and pore water chemical conditions are mediated by microbial processes. Thus, pore water saturation calculations often fail to predict the occurrence of vivianite because they do not adequately represent chemical conditions within sediment microenvironments. In general, the specific role microorganisms play in vivianite formation still remains an open question.

In summary, the formation of vivianite in aquatic sediments constitutes an important process in phosphorus sequestration. Vivianite forms rapidly under reducing conditions in surface freshwater sediments, and new findings from the marine sciences suggest that the mineral may be an important burial sink of phosphorus also in many organic- and iron-rich marine settings. The development of a novel sediment preparation method and the combination of different analytical techniques were key to rendering new findings possible. The present study demonstrates that in future, the development of new analytical approaches aimed at a detailed understanding of the mechanisms underlying vivianite mineral formation in sediments is essential, to better assess the relevance of vivianite in the global P cycle.

Zusammenfassung

In dieser Dissertation wurden das Auftreten und die ökologische Bedeutung Vivianits in Süßwassersedimenten erforscht. Vivianit, $Fe_3(PO_4)_2 \cdot 8\,H_2O$, ist das am weitensten verbreitete reduzierte Eisenphosphatmineral, das sich in Gewässersedimenten bildet. Über die Mechanismen der Vivianitbildung in rezenten Sedimenten und die quantitative Rolle des Minerals für die Speicherung von Phosphor ist bisher wenig bekannt. Eisenoxide und Eisenhydroxide sind in der Lage, Phosphationen effektiv zu binden. Unter anoxischen Bedingungen können diese Verbindungen jedoch gelöst werden. Die Bildung von Vivianit könnte dagegen zu einer signifikanten Speicherung von Phosphor unter reduzierenden Bedingungen beitragen und damit die Bedeutsamkeit des Eisens für den langfristigen Phosphorrückhalt in Sedimenten herausstellen.

Um neue Erkenntnisse zu gewinnen, lag der Fokus zunächst auf der Enwicklung einer Methode, die es erlaubte Vivianit direkt mittels Röntgendiffraktometrie zu identifizieren. Dies gelang nach Anwendung einer Dichtetrennung gefriergetrockneten Sediments mit Hilfe einer Schwerelösung. Dabei kam es zu einer Anreicherung von Vivianitkristallen in der schweren Sedimentfraktion, wobei die Kristalle gut an ihrer blauen Färbung zu erkennen waren. Diese Anreicherung war der Schlüssel für die erfolgreiche Identifikation Vivianits mittels Röntgenpulverdiffraktometrie. Durch Ausnutzen der paramagnetischen Eigenschaften Vivianits gelang es erstmalig, Vivianit in Oberflächensedimenten zu quantifizieren. Die vorliegende Arbeit zeigt beispielhaft, dass Vivianit signifikant, mit 10-40 %, zur Phosphorretention in Süßwassersedimenten beitragen kann.

Die Bildung Vivianits ist im besonderen Maß von der Verfügbarkeit von Fe^{2+}-Ionen im Porenwasser des Sediments abhängig. Die Vivianitbildung ist so lange begünstigt, wie die Versorgung mit Fe^{2+}-Ionen die Produktion von Sulphiden übersteigt. Das molare Schwefel zu Eisen Verhältnis des Sediments wurde als ein wichtiger Indikator für die Bedingungen identifiziert, welche die Triebkräfte für die An- und Abwesenheit Vivianits darstellen. Vivianit trat nur dann auf, wenn das Schwefel zu Eisen Verältnis des Sediments Werte kleiner als 1.1 annahm. Theoretisch ist die Vivianitbildung so lange begünstigt

und nicht durch die Versorgung von Fe^{2+}-Ionen begrenzt, wie das Schwefel zu Eisen Verhältnis einen Wert von 1.5 nicht überschreitet. In diesem Zusammenhang zeigten die Untersuchungen, dass die Eutrophierung von Gewässern und der damit verbundene Anstieg der Sulphidproduktion die Bildung von Vivianit beeinträchtigt, und eine Abnahme des Phosphorbindungsvermögens des Sediments zur Folge hat. Die vorliegende Arbeit macht deutlich, dass eine artifizielle Erhöhung des Eisengehaltes des Sediments im Rahmen einer Seenrestaurierung eine Vivianitbildung induzieren kann und so langfristig zu einer signifikanten Erhöhung des Phosphorrückhaltes führt.

Sättigungsberechnungen ergaben, dass ein hinsichtlich Vivianits übersättigtes Porenwasser kein sicheres Indiz für die Anwesenheit des Minerals ist. Es ergaben sich deutliche Abweichungen zwischen den thermodynamischen Berechnungen und dem eigentlichen Vorkommen des Minerals im Sediment. Da Nukleation und Kristallwachstum auf der Nano- bis Mirometerskala ablaufen und die chemischen Bedingungen im Porenwasser maßgeblich von Mikroorganismen gesteuert werden, liefern Sättigungsberechnungen, die in der Regel auf makroskopischen Messwerten basieren, keine verlässlichen Vorhersagen. Die Berechnungen sind nicht in der Lage die kleinskaligen chemischen Bedingungen im Porenraum des Sediments abzubilden. Welche spezifische Funktion Mikroorganismen bei der Bildung von Vivianit haben, bleibt jedoch weiterhin offen.

Zusammenfassend zeigen die Untersuchungen, dass die Bildung von Vivianit einen wichtigen Prozess der Phosphorbindung in Gewässersedimenten darstellt. Vivianit bildet sich rasch unter reduzierenden Bedingungen in rezenten Süßwassersedimenten und neueste Befunde aus der marinen Forschung deuten darauf hin, dass Vivianit auch in organik-reichen, anoxischen marinen Sedimenten eine wichtige Rolle für die langfristige Bindung von Phosphor spielt. Die Entwicklung einer neuartigen Sedimentpreparation und die Kombination verschiedenster analytischer Techniken machte die in dieser Arbeit vorgestellten neuen Erkenntnisse möglich. Um zukünftig die Relevanz der Vivianitbildung im globalen Phosphorkreislauf besser bestimmen zu können, ist die Entwicklung neuartiger Verfahren zur detaillierten Untersuchung des Bildungsmechanismus Vivianits in Sedimenten ein essentieller Bestandteil.

Contents

Chapter 1

Introduction

1.1 The sedimentary phosphorus cycle

Phosphorus (P) is a key element to all live. It is integral part of nucleic acids and cell membranes. Phosphorus is a functional component of adenosinetriphosphate - the specific compound universally found among living organisms in which chemical energy is stored within cells. Notwithstanding, P plays a key role in the regulation of cell internal reactions facilitated through the phosphorylation and dephosphorylation of specific messenger compounds. Due to these crucial functions in living cells, the availability of P shapes the structure of ecosystems and their productivity as a whole. In aquatic ecosystems, P is the ultimate limiting nutrient governing primary production (Tyrrell, 1999).

Understanding the cycling of P, its dynamics and the role of the sediments in regulating the P availability in the water column have been of particular interest among researchers for almost a century. Due to excessive use of fertilisers in agriculture in the last century, the input of nutrients into freshwaters and coastal seas has led to a mass development of algae with far reaching consequences for the functioning of the ecosystem in its entity, the diversity of the aquatic fauna, and human related ecosystem services such as drinking water supply and the use of the ecosystems for recreational purposes. Although nutrient inputs in Europe have been significantly reduced within the last 30 yr, eutrophication of lakes, rivers and coastal seas is still an important issue (Smith *et al.*, 2006; Withers *et al.*, 2014).

Since all the organic and inorganic material produced within (autochthon-

ous) or transported into (allochthonous) the water is eventually deposited in bottom sediments, the reactions taking place within the sediment are important for the availability of P in the overlying water. Ultimately, it is the balance between sources and sinks which determines the availability of P for primary producers in aquatic systems. In the aquatic realm, next to fluvial and groundwater export, it is the burial in sediments which accounts for the major loss of P (Katsev *et al.*, 2006; Hupfer & Lewandowski, 2008).

The sequestration of P depends on different processes including organic matter decomposition, diffusion of orthophosphate, adsorption-desorption mechanisms and chemosorption (Søndergaard *et al.*, 2001). Furthermore, characteristics of the depositional environment such as the nature of the input source material and the sedimentation rate have an influence on the ability of a sediment to retain P (Ruttenberg, 1992; Moosmann *et al.*, 2006). The chemical transformations taking place are thereby intimately connected with the elemental cycles of iron (Fe) and sulphur (S). In the following the main P transformations in sediments are explained and summarised (Fig. 1.1).

Once organic and inorganic matter sinks through the water column and is accumulating at the bottom, microbially mediated degradation starts. This leads to a liberation of the former organic-bound P and to a release into the water column where it can again be taken up by primary producers. This inorganic form of phosphorus available for primary producers is defined as "orthophosphate" (HPO_4^{2-}/PO_4^{3-}). However, not all the P bound in organic matter is recycled, but a fraction is buried in sediments by refractory organic compounds.

Next to this organic-bound P, the fixation of P can also appear in various distinct inorganic compounds. These include orthophosphate sorbed onto the surface of aluminium hydroxides, clays, calcite and Fe(oxyhydr)oxides (Søndergaard *et al.*, 2001). As long as oxic conditions prevail orthophosphate released during the decomposition of organic matter can be efficiently trapped at the surface of oxidised Fe particles (Einsele, 1936; Mortimer, 1941). However, once oxygen becomes depleted, these oxidised Fe particles are subject to microbially mediated and chemical reduction, leading to a liberation of the former sorbed orthophosphate, and dissolved ferrous Fe (Fe^{2+}). Once

oxic conditions recover, such as during mixing events, Fe^{2+} is re-oxidised, acting as a P trap again. This "reactive" Fe pool can be reversible oxidised and reduced, keeping its function as a binding agent for P. On the contrary, aluminium-bound P is stable under both oxic and anoxic conditions. This is why aluminium salts have been commonly used as measure of lake restoration aimed at the reduction of P levels in the water column of eutrophic lakes (Cooke *et al.*, 2005; Huser *et al.*, 2015).

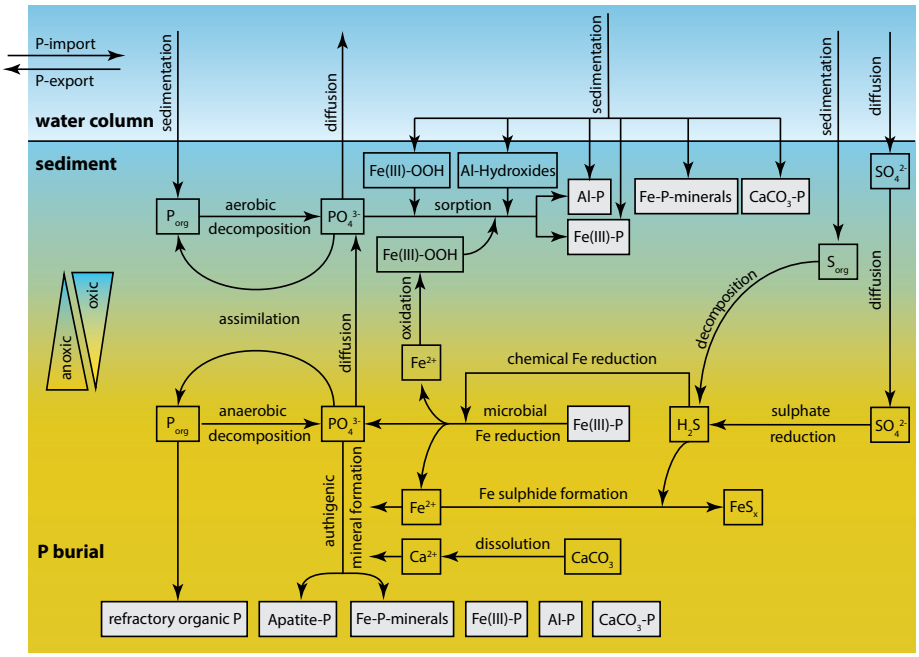

Figure 1.1: Schematic representation of P diagenetic processes in organic-rich freshwater sediments. The main transformations are: (1) microbial decomposition of organic matter, (2) sorption of phosphate on metal oxides and other mineral particles, (3) microbial and chemical reduction of Fe(III)-P compounds including hydrogen sulphide production and Fe sulphide formation, and (4) authigenic formation of reduced Fe-P minerals. Boxes in grey represent P sinks.

By controlling the production of organic matter, P simultaneously exerts strong impact on the oxygen concentration in the water due to the oxygen demanding degradation of organic material. This in turn leads to a positve

feedback regarding the liberation of P from Fe(oxyhydr)oxides at the sediment water interface. Indicative for the coupling of these processes is for example the temporary increase in orthophosphate concentration observed in many lakes' oxygen depleted hypolimnia during summer stratification, which cannot be solely explained by the degradation of organic matter (Nürnberg, 1987; Gächter & Müller, 2003).

Next to oxygen and Fe there are also other alternative electron acceptors used for the oxidation of organic matter. These include inorganic compounds such as nitrate, manganese, sulphate and organic matter (Lau *et al.*, 2014). When sulphate is used as a terminal electron acceptor, this affects the cycling of Fe in the sediment and hence also the binding of P. Since the reduction of sulphate leads to the formation of sulphides (S^{2-},HS^{-}) which are immediately bound by the reaction with metal ions, dissolved Fe (Fe^{2+}) is immobilised through the formation of insoluble Fe sulphides (FeS_x). However, sulphidic bound Fe is not able to bind P and is to a large extend buried in sediments (Morse *et al.*, 1987) if chemical conditions remain anoxic. Simultaneously, Fe(oxyhydr)oxide-P compounds may undergo reductive dissolution in the presence of hydrogen sulphide which leads to a release of orthophosphate into the overlying water (Sugawara *et al.*, 1957; Smolders & Roelofs, 1993; Roden & Edmonds, 1997; Zak *et al.*, 2006). However, in the absence of oxygen, the liberation of Fe^{2+}, orthophosphate, and S^{2-} also leads to elevated concentrations of these solutes in pore waters. This increase in the concentration of solutes favours mineral authigenesis in sediments such as the formation FeS_x, siderite ($FeCO_3$) and reduced Fe phosphate minerals, most prominently vivianite.

Iron associated P compounds have long been considered not to be a significant burial form for P in the long-term. This is due to the iron's redox sensitivity and its immobilisation through free sulphides. However, an increasing number of studies prove the importance of Fe for the burial of P also under anoxic conditions (Jilbert & Slomp, 2013; Kleeberg *et al.*, 2013; Slomp *et al.*, 2013; Dijkstra *et al.*, 2014; Kraal *et al.*, 2014). It has been proposed that this is due to the formation of reduced Fe(II)-P minerals such as vivianite. Those Fe(II)-P minerals are stable under reducing sedimentary conditions and thus

contribute to the sequestration of P in sediments.

1.2 Reduced iron phosphates in anoxic sediments

Phosphorus bound in inorganic compounds which have been forming in a secondary reaction within the sediment or already in the water body are called authigenic P phases. These authigenic phases include Ca-P and Fe(II)-P minerals as well as Fe(oxyhydr)oxide-P compounds which resisted reductive dissolution in the anoxic sediment.

In the marine realm, calcium phosphate such as carbonate fluorapatite, $Ca_{10}(PO_4)_{6\text{-}x}(CO_3)_x(OHF)_{2+x}$, is the most important authigenic sink of P, significantly contributing to the global P burial (Ruttenberg & Berner, 1993; Paytan & McLaughlin, 2007). Apatite has been found in a varity of environmental settings and its formation is considered to be biogenic (Omelon *et al.*, 2013).

In contrast to calcium and calcium phosphates, the role of Fe in P sequestration, and in particular the processes leading to long-term retention of Fe associated P compounds under anoxic sedimentary conditions remain largely unclear. There are two main different Fe-P compounds in anoxic sediments: first, there are oxidised Fe particles and mixed valence Fe(II)/Fe(III) compounds which act as sorption agents for orthophosphate or bind orthophosphate in their crystall lattice. These phases have been found in reducing sediments (Hyacinthe & Van Cappellen, 2004; Lehtoranta *et al.*, 2009), suggesting a preservation from reduction due to a lack of readily degradable organic matter or due to protective coatings of Fe sulphides (FeS_x) (De Vitre *et al.*, 1988). Second, there is the formation of reduced Fe(II)-P minerals, such as vivianite ($Fe_3(PO_4)_2 \cdot 8\,H_2O$).

Vivianite is the most common reduced Fe(II) phosphate in freshwater sediments (Nriagu, 1972; Berner, 1981b), and represents the Fe-rich end-member of the vivianite mineral group ($M_3(XO_4)_2 \cdot 8\,H_2O$, where M= divalent Mg, Mn, Fe, Co, Ni, Cu, Zn, and X=P or As). The mineral is named after the English mineralogist John Henry Vivian (1785-1855) and crystallizes in the monoclinic system. Vivianite is paramagnetic but undergoes antiferromag-

netic transition at a Néel temperature of 12 K (Meijer *et al.*, 1967; Frederichs *et al.*, 2003). Unoxidised, pristine vivianite is colourless and translucient. However, upon exposure to air vivianite becomes intensively blue in colour which is due to a partial oxidation of Fe^{2+} in the vivianite lattice (Hush, 1967). In this surface-oxidised state, vivianite is almost indefinitely stable at room temperature (Nriagu, 1972). Vivianite further oxidises to poorly crystalline ferric or mixed valence ferrosoferric phosphate phases at temperatures above 50 °C (Nriagu, 1972; Nriagu & Dell, 1974; Pratesi *et al.*, 2003).

Vivianite has been reported from various settings all over the world including freshwater and marine sediments, waterlogged soils, bogs, archaelogical settings, waste water sludges and hydrothermal deposits. As ferric Fe phases and organic matter serve as source material for Fe^{2+} and orthophosphate in pore waters, vivianite often occurs in the vicinity of these phases. Crystal aggregates of vivianite reported in literature were of needle or spherical shape and ranged from a few micrometres to several centimetres in diameter. The mineral is stable under pH conditions ranging between 6 and 9 (Nriagu, 1972). High Fe^{2+} and orthophosphate concentrations often found in anoxic non-sulfidic environments favour the precipitation of the mineral (Nriagu & Dell, 1974; Nriagu, 1972). However, already Emerson & Widmer (1978) demonstrated by flux calculations that the formation of crystals cannot be explained by thermodynamic mineral equilibria alone, and hence there is no equilibrium control by vivianite with respect to pore water orthophosphate and Fe^{2+} concentrations (Postma, 1981). Recently, Walpersdorf *et al.* (2013) showed that the concentration of orthophosphate in an anoxic meadow soil was not controlled by the occurrence of vivianite.

The majority of vivianite findings have been made in freshwater systems (e.g. Hearn *et al.*, 1983; Nembrini *et al.*, 1983; Manning *et al.*, 1991; Taylor *et al.*, 2008; Nanzyo *et al.*, 2013; Cosmidis *et al.*, 2014; O'Connell *et al.*, 2015). In the marine realm, although direct mineral proofs are generally sparse, vivianite formation appears to be more restriced than in freshwater systems (Berner, 1981a). On the one hand, this might be due to higher sulphate concentrations in marine waters in comparison to freshwaters. A higher supply with sulphate results in a higher potential for the production of

sulphides favouring the immobilization of Fe through the formation of FeS_x, and hence lower Fe^{2+} concentration in pore waters. On the other hand, the precipitation of calcium phosphates may be favoured in comparison to Fe phosphates because of elevated Ca^{2+} concentration in the ocean. However, recent studies from anoxic and even sulphidic water bodies report significant amounts of P associated with Fe (März *et al.*, 2008; Kraal *et al.*, 2012; Jilbert & Slomp, 2013; Slomp *et al.*, 2013; Dijkstra *et al.*, 2014). Finally, Hsu *et al.* (2014) and Egger *et al.* (2015) found vivianite nodules directly below the sulphate-methane transition zone (SMTZ) in deep sea and coastal sediments rich in organic matter and Fe.

Based upon microbial batch-culture experiments, it has been shown that microorganisms are able to direct the precipitation of an assemblage of secondary mineral phases, such as siderite, apatite, magnetite and vivianite depending on the concentration of solutes in the culture medium and redox conditions (Fredrickson *et al.*, 1998; Glasauer *et al.*, 2003). These findings indicate that microorganisms are actively involved in the formation of vivianite. Through the development of cell-mediated microenvironments, the formation of different secondary mineral phases can be favoured in close proximity to each other. However, the mechanisms behind vivianite nucleation and the extent to which microorganisms direct the precipitation of the mineral still includes a lot of questions.

A group of microorganisms are able to accumulate polyphosphates and may trigger the formation of reduced Fe phosphate minerals in sediments (Cosmidis *et al.*, 2014). These microorganisms store polyphosphates under oxic conditions but hydrolyse these compounds during anoxic conditions to gain energy. This leads to locally enhanced orthophosphate concentrations. It has been proposed that calcium phosphate formation in the ocean may result from the activity of these bacteria (Schulz & Schulz, 2005; Omelon *et al.*, 2013). Thus, in anoxic waters with high Fe^{2+} concentration, polyphophate accumulating bacteria could play a significant role in the formation of reduced Fe(II) phosphates and vivianite formation (Hupfer *et al.*, 2007).

In laboratory studies it has been shown that vivianite appears as a secondary mineral product following Fe(III) reduction by dissimilatory Fe reducing

bacteria (DIRB) if sufficient inorganic phosphate was present in the culture medium (Fredrickson *et al.*, 1998; Glasauer *et al.*, 2003; Borch & Fendorf, 2007; O'Loughlin *et al.*, 2013). These studies suggest that hydrous ferric oxide (HFO) and sulphate green rust are important precursor compounds from which vivianite eventually forms. In marine sediments, vivianite grains were detected within cells of sulphate-reducing *Deltaproteobacteria*. These bacteria are believed to mediate the anaerobic oxidation of methane with sulphur in a consortium with methanotrophic archaea (Milucka *et al.*, 2012), and apparently accumulate Fe- and P-rich granules within their cells.

Vivianite formation is not only restricted to the sediments but it has been shown to form also on sinking particles (Cosmidis *et al.*, 2014) in a meromictic lake having exceptionally high Fe^{2+} and orthophosphate concentrations (up to 1200 μmol L^{-1} and 300 μmol L^{-1}, respectively) in the monimolimnion. It has been proposed that vivianite nodules originate through topotactic conversion from mixed valence Fe(II)-Fe(III) phosphates formed at the oxic-anoxic interface (redoxcline) while sinking through the anoxic water column. At the sediment surface, the combined release of orthophosphate by the degradation of organic matter, polyphosphate accumulating bacteria, the reduction of Fe(oxyhydr)oxides-P compounds, liberation of Fe(II)-Fe(III)-P compounds as well as groundwater P input sustains exeptionally good conditions for vivianite formation (Schettler *et al.*, 2007; Cosmidis *et al.*, 2014).

All these findings from natural sediments, soil incubations and batch culture experiments indicate that vivianite formation in sediments is the result of multiple factors and processes. The interplay between the availability of source material (ferric Fe phases and fresh oranic matter), the extend of competing reactions, such as sulphate reduction and FeS_x formation as well as resorption processes, and the activity of microorganisms, including the development of cell-mediated microenvironments, play an important role in vivianite formation. Despite of the regular occurrence of vivianite in sedimentary cores (e.g. Brauer *et al.*, 1999; Fagel *et al.*, 2005; Sapota *et al.*, 2006; Minyuk *et al.*, 2013) the formation of vivianite and the factors controlling its occurrence in surface sediments are sparsely investigated. Apart from the fact that vivianite is not uncommon in sediments, it remains open to which extend

vivianite contributes to P immobilization during early sediment diagenesis.

One reason why there is limited knowledge about the factors controlling the natural occurrence of the mineral and its quantitative importance in P sequestration are technical challenges regarding the direct and unambiugous identification of vivianite. Since P is only a minor constituent in sediments, and a large fraction of total P can be organic or sorbed P, vivianite may comprise only a small part of the inorganic sediment matrix (Lindsay *et al.*, 1989). Thus, the identification of vivianite within a sediment matrix is difficult.

The application of X-ray diffraction in order to directly identify vivianite has been regarded not productive, because of the minerals immidiate oxidation to an X-ray amorphous phase after contact with air (März *et al.*, 2008). These technical difficulties may also explain why indirect measures, such as pore water equilibrium calculations and sequential P extraction procedures, have been a widely used tool in trying to predict vivianite occurrence in sediments. However, these indirect approaches can only give a rough evaluation of the general conditions which may or may not indicate vivianite occurrence. Thus, the validity and specificity of findings regarding vivianite occurrence and the potential factors and processes indicating conditions that are important drivers behind mineral formation are truly limited.

1.3 Objectives and outline

In the preceding paragraphs the functioning of Fe in binding P in sediments, and importantly the nature and occurrence of the ferrous Fe phosphate mineral vivianite have been presented. Although vivianite is a common authigenic mineral in (freshwater) sediments, much remains unknown about vivianite and its quantitative importance in P sequestration.

The aims of this thesis are to advance our understanding of the processes leading to P burial under reducing and Fe-rich conditions, and in particular to evaluate the role of vivianite in P sequestration. In this thesis a new approach is presented allowing the direct identification of vivianite in surface sediments using powder X-ray diffraction. Benefiting from these technical advances, basic characteristics of the crystal aggregates, factors controlling the occurrence of

the mineral and the quantitative importance of vivianite in three different lakes are presented. To render these new insights possible, a set of analytical approaches, including microscopic, chemical, physical and magnetic methods are combined in this thesis. In the following chapters, the new findings are presented in detail in form of three peer-reviewed manuscripts.

The first manuscript "Evidence for vivianite formation and its contribution to long-term phosphorus retention in a recent lake sediment: a novel analytical approach" involves the study of an organic-rich surface sediment, artificially enriched in Fe as a former measure of lake restoration (Lake Groß-Glienicke, Germany). The application of a heavy-liquid separation of dry sediment is introduced, representing an efficient tool for the identification of vivianite within a sediment matrix.

Vivianite crystal aggregates are identified by combining powder X-ray diffraction and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. It is shown that contact with air does not impede the identification of vivianite and the crystal aggregates are surface oxidised only. Pore-water chemical conditions according to sediment depth are presented and subsequent equilibrium calculations are used to specify the saturation state of the pore water with respect to vivianite. Saturation calculations and the actual occurrence of the mineral in different sediment depths are compared.

The contribution of vivianite to P retention is, for the first time, evaluated using two complementary methods, as there are chemical digestion and magnetic hysteresis measurements of sediment samples enriched in vivianite. The study shows that vivianite is a significant burial form of P in surface sediments under reducing sedimentary conditions, and that the formation of the mineral is triggered by an artifical Fe amendment, more than 20 years ago.

In the second manuscript "Sedimentary sulphur:iron ratio indicates vivianite occurrence: a study from two contrasting freshwater systems" the occurrence of vivianite is studied in sediments of a deep, eutrophic, Fe-poor lake

(Lake Arendsee, Germany) as well as in a shallow, eutrophic Fe-rich riverine lake (Lower Havel, Germany). The application of the before mentioned heavy-liquid separation is shown to be a simple and effective approach leading to an enrichment of vivianite nodules in the high-density samples. This separation procedure forms the basis for the direct identification of the mineral in both waters.

A comparison of vivianite layers with the depth-profile course of sedimentary S, Fe and P content is presented. Moreover, a speciation regarding the P and S forms in the sediment and the extractions characteristics of pure as well as naturally born vivianite nodules is presented. From those results, the sedimentary molar S:Fe ratio is identified to indicate conditions that are important drivers behind vivianite formation. Vivianite was present only at low molar S:Fe ratios, i.e. if the production of Fe^{2+} exceeded that of S^{2-}. The analysis revealed, that in course of increasing primary production, sulphide formation and the immobilisation of reactive Fe species is intensified, leading to lower or no vivianite formation.

In the third manuscript, "A review on the occurrence, identification and environmental relevance of vivianite in soils and sediments" the findings of the former two research articles are connectedly discussed and embedded in a synthesis of previously published literature in form of a review-article. This review gives a comprehensive overview on vivianite formation in soils and sediments, its methodological identification, its appearance and the features of its occurrence.

Including recent findings from lacustrine and coastal marine systems as well as from microbial batch culture experiments, microorganisms appear to control the formation of vivianite in natural sediments. Through the activity of bacteria, microenvironments evolve within the sediment matrix providing protected pore voids in which vivianite and other authigenic mineral phases form in close proximity to each other. This might explain why thermodynamic equilibrium calculations often fail to predict vivianite occurrence. Those calculations are based upon bulk pore water characteristics which do not represent chemical conditions of single micrometre-sized pore voids within a sediment.

The development of such microenvironments favourable for vivianite formation is in turn controlled by the supply of organic matter and Fe. Vivianite authigenesis occurs only if the production of Fe^{2+} exceeds that of S^{2-} and sufficiently high P_i is available. Those sedimentary environments were classified as "anoxic, non-sulfidic" and indeed, vivianite has been regularly detected in such environments. Recently, vivianite has been identified in organic-rich coastal surface sediments of the Bothnian Sea, where vivianite formation is closely associated with the anaerobic oxidation of methane. These findings suggest that vivianite plays an important role in P sequestration also in the marine realm which has so far largely been ignored.

In the last chapter, the main results of this thesis are summarized and discussed, and conclusions are given.

Chapter 2

Evidence for vivianite formation and its contribution to long-term phosphorus retention in a recent lake sediment: a novel analytical approach

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2.1 Abstract

Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, is a ferrous iron phosphate mineral which forms in waterlogged soils and sediments. The phosphorus (P) bound in its crystal lattice is considered to be immobilised because vivianite is stable under anoxic, reducing, sedimentary conditions. Thus, vivianite formation can make a major contribution to P retention during early diagenesis. Much remains unknown about vivianite in sediments, because technical challenges have rendered direct identification and quantification difficult. To identify vivianite and assess its significance for P burial during early diagenesis we studied the consequences of a 1992/1993 in-lake application of $FeCl_3$ and $Fe(OH)_3$ aimed at restoring Lake Groß-Glienicke (Berlin, Germany). In a novel approach, we firstly applied a heavy-liquid separation to the iron-rich surface sediments which allowed direct identification of vivianite by X-ray diffraction in the high-density ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$) sediment fraction. Secondly, we assessed the contribution of vivianite to P retention, combining results from chemical digestion with magnetic susceptibility data derived from magnetic hysteresis measurements. Scanning electron microscopy revealed that the dark blue spherical vivianite nodules were 40–180 μm in diameter, and formed of platy- and needle-shaped crystal aggregates. Although equilibrium calculations indicated supersaturation of vivianite throughout the upper 30 cm of the sediment, the vivianite deposits were homogeneously distributed within, and restricted to, the upper 23 cm only. Thus, supersaturated pore water alone cannot serve as a reliable predictor for the in situ formation of vivianite. In Lake Groß-Glienicke, vivianite formation continues to be triggered by the artificial iron amendment more than 20 yr ago, significantly contributing to P retention in surface sediments.

2.2 Introduction

Understanding phosphorus (P) dynamics in aquatic ecosystems has been of particular interest among researchers for almost a century. Since P is an important nutrient limiting primary production, the cycling of P, and the role of the sediments in regulating P availability in the water column have been

studied intensively. Long-term burial of P in sediments is the only mechanism able to shield P from continuous (re)-cycling, and therefore represents an output of P from the internal nutrient cycle (Katsev *et al.*, 2006; Hupfer & Lewandowski, 2008).

The burial of P depends on several processes (Ruttenberg, 1992; Søndergaard *et al.*, 2001) and fixation is of either organic or inorganic phases. Organic P originates from settled organic material which is refractory or not yet mineralised by microorganisms. Inorganic phases include P sorbed onto the surface of iron(oxy)hydroxides, aluminium hydroxides, clays and calcite (Moosmann *et al.*, 2006). P associated with Fe(III) minerals have been found in anoxic marine and estuarine sediments, indicating a resistance towards reductive dissolution of these compounds, at least under non-sulfidic conditions (Hyacinthe & Van Cappellen, 2004; Lehtoranta *et al.*, 2009). Thus, during sediment diagenesis there may be the formation of stable phosphate minerals which bind P in their crystal lattice and contribute to permanent P burial (see e.g. Jilbert & Slomp, 2013). However, the processes controlling the P burial under anoxic conditions are still not fully understood (e.g. Stigebrandt *et al.*, 2013).

One specific phosphate mineral which forms during sediment diagenesis is the ferrous phosphate vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$. The mineral is a regularly found deposit in sedimentary cores (e.g. Brauer *et al.*, 1999; Fagel *et al.*, 2005; Sapota *et al.*, 2006; Minyuk *et al.*, 2013). Since P is only a minor constituent in sediments, the direct identification of vivianite is difficult. While a large fraction of total P can be organic or sorbed P, vivianite may comprise only a small part of the inorganic sediment matrix (Lindsay *et al.*, 1989).

In natural systems, vivianite is stable under pH conditions from 6 to 9 (Nriagu, 1972) and can form in waterlogged soils and sediments (Berner, 1981b). The precipitation of vivianite directly from pore water solution is favoured by high concentrations of ferrous iron (Fe(II)) and soluble reactive P (SRP) often found in anoxic non-sulfidic environments (Nriagu, 1972; Nriagu & Dell, 1974; Roden & Edmonds, 1997). By flux calculations Emerson & Widmer (1978) demonstrated that mineral formation is surface- rather than diffusion-controlled, and hence there is no equilibrium control by vivianite

with respect to pore water SRP and Fe^{2+} concentrations (Postma, 1981). Recently, Walpersdorf *et al.* (2013) confirmed that vivianite does not control phosphate solubility in an anoxic meadow soil.

The literature has reported vivianite crystal aggregates to be needle-shaped or spherical with diameters ranging between a few micrometres to several centimetres. Upon exposure to air, the crystals turn vivid blue due to partial oxidation of Fe^{2+} (Hush, 1967). As ferric iron (Fe(III))-phases and organic matter serve as source material for Fe^{2+} and SRP, vivianite often occurs in the vicinity of these phases. Laboratory studies show that vivianite appears as a secondary mineral product following Fe(III) reduction by dissimilatory iron-reducing bacteria (DIRB) if sufficient PO_4^{3-} is present in the culture medium (e.g. Borch & Fendorf, 2007; O'Loughlin *et al.*, 2013).

All these findings indicate that the interplay between the availability of source materials (Fe(III)-phases, organic matter), the activity of DIRB and their cell-mediated microenvironments, as well as the pore structure of the sediment matrix, are important in vivianite formation. However, direct evidence of vivianite in recent sediments (e.g. Nembrini *et al.*, 1983; Hearn *et al.*, 1983; Manning *et al.*, 1991; Taylor *et al.*, 2008; Nanzyo *et al.*, 2013) appears to be scarce. Often the claim of vivianite findings is solely based upon indirect measures, such as equilibrium calculations, sequential P extractions, or electron microprobe analysis lacking direct identification. The difficulty in identifying vivianite in a sediment matrix might be a reason why there is limited knowledge about the quantitative importance of vivianite formation in P burial during early diagenesis.

To address this need, the aims of our present study were to: (1) identify vivianite crystal aggregates from recent lake sediment showing favourable formation conditions in the pore water, (2) determine the significance of vivianite formation for P burial during early diagenesis, and (3) assess the impact of artificial addition of Fe during lake restoration as a trigger for vivianite formation. For these purposes we developed and applied a novel analytical approach, combining heavy-liquid separation of surface sediments followed by mineral identification by X-ray diffraction, elemental analyses and magnetic hysteresis measurements.

2.3 Material and methods

2.3.1 Study site

Lake Groß-Glienicke is a dimictic lake located southwest of Berlin, Germany (52°27′57″ N, 13°06′39″ E), with a mean depth of 6.8 m, a maximum depth of 11 m, and a surface area of 0.67 km^2. Until 1992 the lake was highly eutrophic, and had on average total P (TP) and chlorophyll *a* (Chl *a*) concentrations of 485 $\mu g\,L^{-1}$ and 41 $\mu g\,L^{-1}$ (1989–1992) (Kleeberg *et al.*, 2013). To reduce the P concentration in the water column, the lake was treated with solid ferric hydroxide ($Fe(OH)_3$) and dissolved ferric chloride ($FeCl_3$) between December 1992 and February 1993 (Wolter, 2010). Due to decreased external P inputs and the in-lake P precipitation, TP and Chl *a* decreased reaching today's mesotrophic levels of TP 20 $\mu g\,L^{-1}$ and Chl *a* 7 $\mu g\,L^{-1}$. Sediment stratigraphy shows a distinct increase in Fe and P content corresponding to the time of the in-lake treatment. Today, this shift is evident at a sediment depth of 23 cm. Both Fe and TP contents in the sediment almost doubled after the treatment, reaching 33 $mg\,g^{-1}$ dry weight and 2.6 $mg\,g^{-1}$ dry weight (Kleeberg *et al.*, 2012). Due to the iron's redox sensitivity iron and TP contents are higher throughout the newly formed sediment which has accumulated since the in-lake treatment in 1992/93.

2.3.2 Sample collection and preparation

Porewater

To document the geochemical conditions within the upper 30 cm of the sediment, we used two in situ dialysis samplers (Hesslein, 1976) each with 14 chambers and a vertical resolution of 4 cm. The samplers were filled with deionised water and covered by a 0.2 μm membrane filter (Gelman® HT 200 Tuffryn). To remove oxygen from the chamber water the samplers were degassed with nitrogen for 24 h and subsequently deployed at the deepest site in the lake for 20 d in September 2013 during thermal stratification.

Sediment

Sediment cores 35–40 cm long and 60 mm in diameter were taken in September 2012 and May 2013 by a gravity corer (UWITEC) at the deepest site in the lake. Two hours after sampling the cores were extruded, immediately sectioned into 20 mm slices, frozen, and freeze-dried for at least 72 h. The freeze-dried sediment served as raw material for further analysis and is in the following text referred to as "bulk" sediment.

Subsamples of freeze-dried sediment (about 1 g dry weight) were homogenised by gentle pestling in an agate mortar, and subsequently sieved through 80 μm and 63 μm stainless steel meshes. Only the largest size fraction ($\geq$ 80 μm) was used and thereafter separated by density using two different concentrations of a sodium polytungstate solution ($3\,Na_2WO_4 \cdot 9WO_3 \cdot H_2O$, ABCR). In step I, a sediment sample of approximately 0.3 g was mixed in a centrifuge tube with 10 mL of sodium polytungstate solution (density $\rho = 1.9\,g\,cm^{-3}$) and placed in an ultrasonic bath for 20 min. After sonication the mixture was centrifuged for 10 min at 9.050 rcf. The heavy fraction was then transferred into a new tube. The light fraction and the supernatant were again sonicated for 10 min and then centrifuged for 10 min at 9.050 rcf and the heavy fraction transferred to a new tube. This process was repeated a third time and the heavy fractions of all three runs were pooled. In step II, the pooled heavy fractions from step I were mixed with a sodium polytungstate solution (density $\rho = 2.3\,g\,cm^{-3}$) and processed analogously to step I. Subsequently, each of the three separated sediment fractions (A: $\rho > 2.3\,g\,cm^{-3}$, B: $2.3\,g\,cm^{-3} > \rho > 1.9\,g\,cm^{-3}$, C: $\rho < 1.9\,g\,cm^{-3}$) were rinsed with deionised water until conductivity dropped below 50 $\mu S\,cm^{-1}$, and then freeze-dried. In the following, sediment samples from fraction A ($\rho > 2.3\,g\,cm^{-3}$) were analysed and are referred to as "high-density" samples.

2.3.3 Analysis

Porewater

Subsamples from each dialysis chamber were taken for the analysis of 13 parameters: 6 cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}), 3 anions (Cl^-, SO_4^{2-}, NO_3^-), dissolved inorganic carbon (DIC), free sulfides (HS^-), SRP and ammonia (NH_4^+). Temperature and pH were measured in each chamber using a pH electrode (Mettler Toledo).

Quick sampling and fixation with hydrochloric acid prevented oxidation of redox-sensitive species (Fe^{2+}, Mn^{2+}). Cations were analysed by inductively coupled plasma atomic emission spectrometry (ICP-OES, iCAP 7000series, Thermo Scientific). Anions were analysed by ion chromatography (Shimadzu). Subsamples for DIC were stored in nitrogen-flushed air-tight vessels and analysed on the day of collection using a carbon analyser (multi N/C 3100, Jena Analytics). To prevent oxidation of free sulfides subsamples from each chamber were immediately fixed with 0.2 M zinc acetate solution. HS^- was measured photometrically by applying the methylene blue method (Cline, 1969). Concentrations of SRP and NH_4^+ were determined photometrically by the molybdenum blue method (Murphy & Riley, 1962) and the indophenol method (Bolleter *et al.*, 1961) respectively, using segmented flow analysis (Skalar Scan^{++}, Skalar Analytical B.V.). All determinations were performed in duplicate.

Sediment

The concentrations of Fe, Ca, Al, Mg, Mn, S and P were determined by ICP-OES after wet digestion (HCl 36 %, HNO_3 76 %, volumetric ratio 1 : 3) in a high-pressure microwave oven (Gigatherm). Mineral composition of sediment was characterised by powder X-ray diffraction (XRD) with a Bruker AXS D8 diffractometer equipped with Cu-K_α-radiation and a Sol-X solid state detector. Synthetic, slightly oxidised (blue appearance) vivianite powder (Dr Paul Lohmann GmbH KG) served as an internal XRD standard. The XRD patterns were measured between 5 and 60 ° 2θ with a step of 0.05 ° 2θ and an

integration time of 12 s. Scanning electron micrographs of sediment concretions were obtained with a FEI Quanta 600FEG field emission environmental scanning electron microscope (FE-ESEM). Sediment concretions were sputter coated with palladium prior to the analysis of elemental composition by energy dispersive X-ray spectroscopy at 15 kV acceleration voltage (Jeol-7500F scanning electron microscope) with an EDX detector (X-Max, Oxford Instruments).

Magnetic hysteresis measurements (magnetisation vs. magnetic field) of subsamples of bulk sediment and high-density samples ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$; sample mass ranging from about 1 to 5 mg) were conducted on an Alternating Gradient Magnetometer (Princeton Measurement Corporation) at room temperature in peak fields of 0.3 T (Flanders, 1988). Diamagnetic matter, such as calcium carbonate and quartz, demonstrates a weak negative linear dependency of induced magnetisation on the ambient magnetic field. In contrast, paramagnetic substances, such as many Fe-bearing minerals, including vivianite, show a strong and positive linear dependency of induced magnetisation on the ambient magnetic field. Finally, ferrimagnetic minerals such as magnetite exhibit a much stronger and non-linear field dependency. Their magnetisation curve is called the hysteresis loop.

The proportional factor between magnetisation and magnetic field is named magnetic susceptibility. This characteristic is field independent, i.e. linear, for dia- and paramagnetic substances, and field dependent in the case of ferrimagnetic substances. Thus, paramagnetic susceptibility may be deduced from hysteresis measurements, by calculating the slope of the increasing linear part of the hysteresis loop after magnetic saturation of ferrimagnetic minerals in sufficiently strong magnetic fields. Magnetic hysteresis measurements therefore allow the determination of paramagnetic susceptibility even in the presence of magnetically much stronger ferrimagnetic minerals.

2.3.4 Thermodynamic calculations

Geochemical equilibrium calculations were based on the results of the pore water analysis using the computer program PhreeqC (version 2.18.5570) (Parkhurst & Appelo, 1999) with minteq4 database. The database was extended to include metal complexation with dissolved organic carbon (DOC). The equilibrium constants ($\log K$) for $1:1$ metal-ligand complexes (e.g. Ca-, Fe(II)-fulvic ligand complexes) were taken from Steinmann & Shotyk (1997). The solubility constant of vivianite ($K_{\mathrm{viv}} = 1 \times 10^{-36}$) was taken from Nriagu (1972).

2.4 Results

2.4.1 Chemical conditions in the pore water

There were distinct gradients in pH and concentrations of DIC, NH_4^+, SRP, Fe^{2+} and SO_4^{2-} across the sediment–water interface (SWI) (Fig. 2.1). The pH increased in the water body above the SWI from pH = 7.60 at −23 cm to pH = 8.00 at the SWI, and decreased to pH = 7.15 at 29 cm sediment depth (Fig. 2.1a). The concentration of DIC was almost constant at 3.9 mmol L^{-1} in the overlying 23 cm of the water body above the SWI, and increased to 6 mmol L^{-1} within the upper 4 cm of the sediment and continuously increased down-core to reach 7.9 mmol L^{-1} at 29 cm sediment depth (Fig. 2.1b). SRP concentration increased in the water body above the SWI from 0.15 mmol L^{-1} at −23 cm to 0.25 mmol L^{-1} at −3 cm. Directly at the SWI, SRP had a local maximum concentration of 0.59 mmol L^{-1} and increased further downcore to reach 0.87 mmol L^{-1} at 29 cm sediment depth (Fig. 2.1c). Concentration profiles of NH_4^+ and Fe^{2+} had a similar course: in the water body above the SWI concentrations were almost constant at 0.1 mmol L^{-1} and 0.08 mmol L^{-1}, respectively, and increased by a factor of two and five respectively within the uppermost 4 cm of the sediment (compared to their concentrations at the SWI). Further down-core the concentrations increased to 0.74 mmol L^{-1} and 0.20 mmol L^{-1} at 29 cm (Fig. 2.1c and d). The SO_4^{2-} concentration showed a decreasing sigmoidal trend across the SWI, and from 4 cm below the SWI

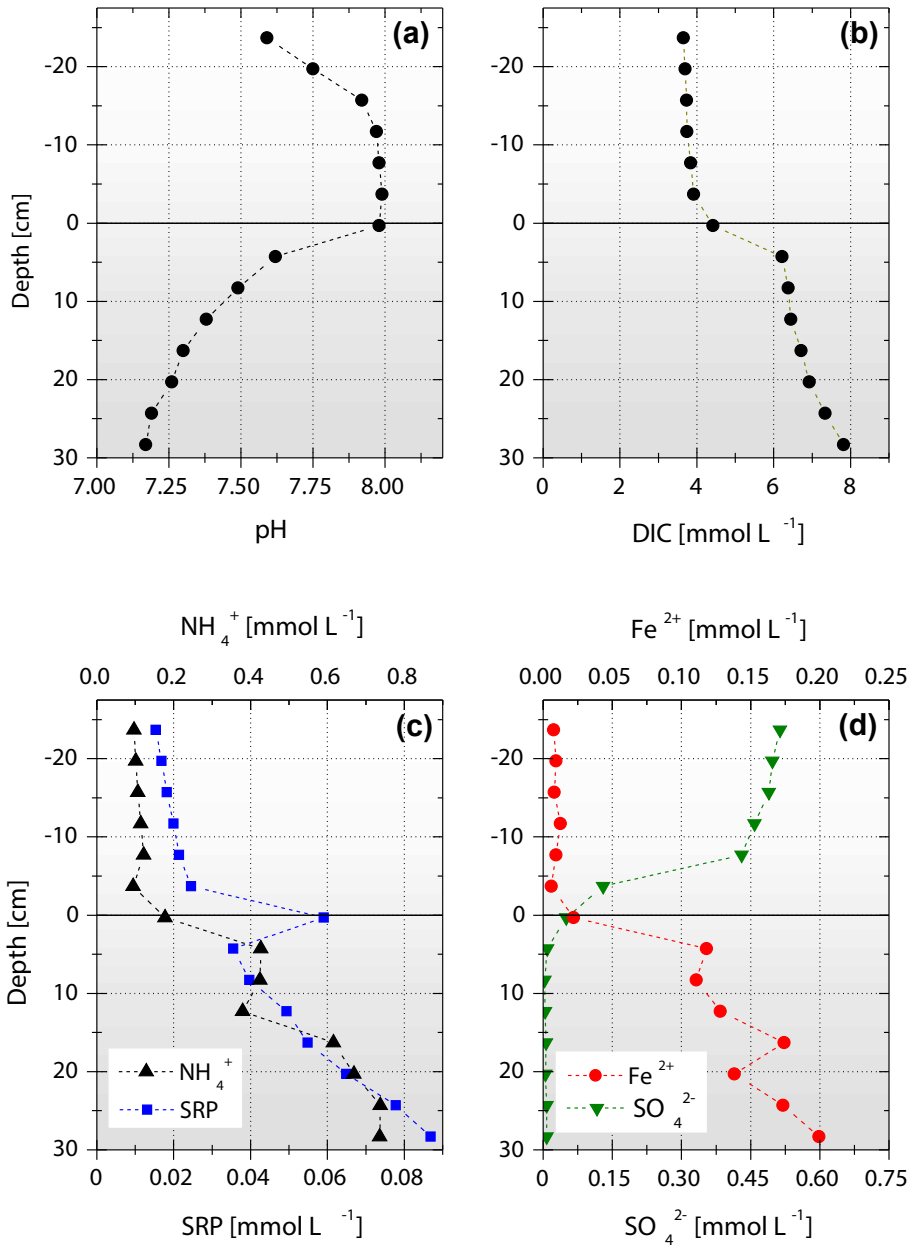

Figure 2.1: Vertical profiles of six parameters taken from an in situ pore water sampler deployed at the deepest point of Lake Groß-Glienicke (positive downward sampling depth) (September 2013): **(a)** pH, **(b)** dissolved inorganic carbon (DIC), **(c)** soluble reactive phosphorus (SRP) and ammonia (NH_4^+), **(d)** ferrous iron (Fe^{2+}) and sulfate (SO_4^{2-}). A depth of 0 cm indicates the sediment–water interface.

and deeper, the concentration was so low as to be close to the detection limit ($0.001\,\mathrm{mmol\,L^{-1}}$) (Fig. 2.1d). The concentrations of HS^- and NO_3^- were not detectable.

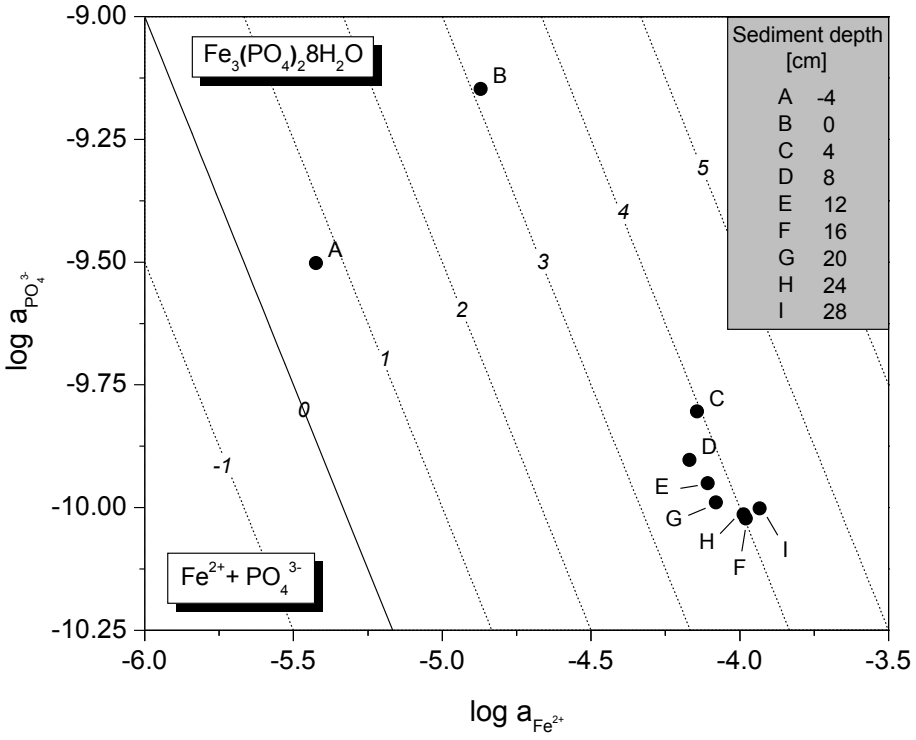

Figure 2.2: Degree of saturation of the pore water with respect to vivianite of Lake Groß-Glienicke in nine different sediment depths (A–I) (September 2013). Letters next to data points indicate sampling depth (positive downward sampling depth). The thick line in the diagram represents the vivianite solubility constant $K_{\mathrm{viv}} = 1 \times 10^{-36}$ given by Nriagu (1972).

The pore water of the sediment was supersaturated with respect to Fe(III) and mixed Fe(III)/Fe(II) phases, including magnetite, hematite, goethite and lepidocrocite. According to our equilibrium calculations, saturation indices (SI) were highest for magnetite and lowest for lepidocrocite (SI = 12.9 and 2.7, respectively) and slightly decreased with sediment depth. For vivianite, in the pore water of the sediment, there was continuous supersaturation of

four orders of magnitude at depths of 4–28 cm (Fig. 2.2). At the SWI, the supersaturation of vivianite was about one order of magnitude lower than in subjacent pore fluids (4–28 cm), and 4 cm above the SWI the supersaturation was close to equilibrium. There was a sharp increase in the activity of Fe^{2+} ($a_{Fe^{2+}}$) with sediment depth, as shown by plotting $a_{Fe^{2+}}$ against that of $a_{PO_4^{3-}}$ (Fig. 2.2). The thermodynamic calculations showed a strong subsaturation for manganese phosphate ($SI \leq -10$), saturation close to equilibrium for siderite ($FeCO_3$) and supersaturation for the calcium phosphate hydroxylapatite (SI ranged from 8 to 10) in the upper 28 cm of the pore water of the sediment.

To determine the effect of dissolved organic carbon (DOC) on the output of the equilibrium calculations, and in particular on $a_{Fe^{2+}}$ (see e.g. Reuter & Perdue, 1977), we performed equilibrium calculations with DOC concentrations ranging from 10 to 500 mg L^{-1}. The results showed that there is a significant decrease in $a_{Fe^{2+}}$ through the formation of Fe(II)–organic-ligand complexes only at DOC concentrations above 200 mg L^{-1}. As this threshold concentration is at least one order of magnitude higher than those found in the water column of Lake Groß-Glienicke, we did not include DOC as input data for equilibrium modelling.

2.4.2 Structural and elemental composition of sediments

The XRD patterns from different sediment depths showed quartz and calcium carbonate phases as well as several other minerals, e.g. dolomite, plagioclase and pyrite (for clarity not indicated in Fig. 2.4a) to be present in the sediment. However, the XRD reflexes characteristic for vivianite could not be identified from bulk sediment samples. The diffraction pattern of synthetic vivianite powder (blue appearance) was in coincidence with the vivianite reference pattern which use data from the Crystallography Open Database (COD). The synthetic vivianite powder changed its colour from dark blue to orange-brown and lost its characteristic diffraction pattern upon heating at 60 °C for 24 h (Fig. 2.4a).

Examination of sediment with a reflected-light microscope revealed that dark blue nodules were present throughout the upper 23 cm of the sediment,

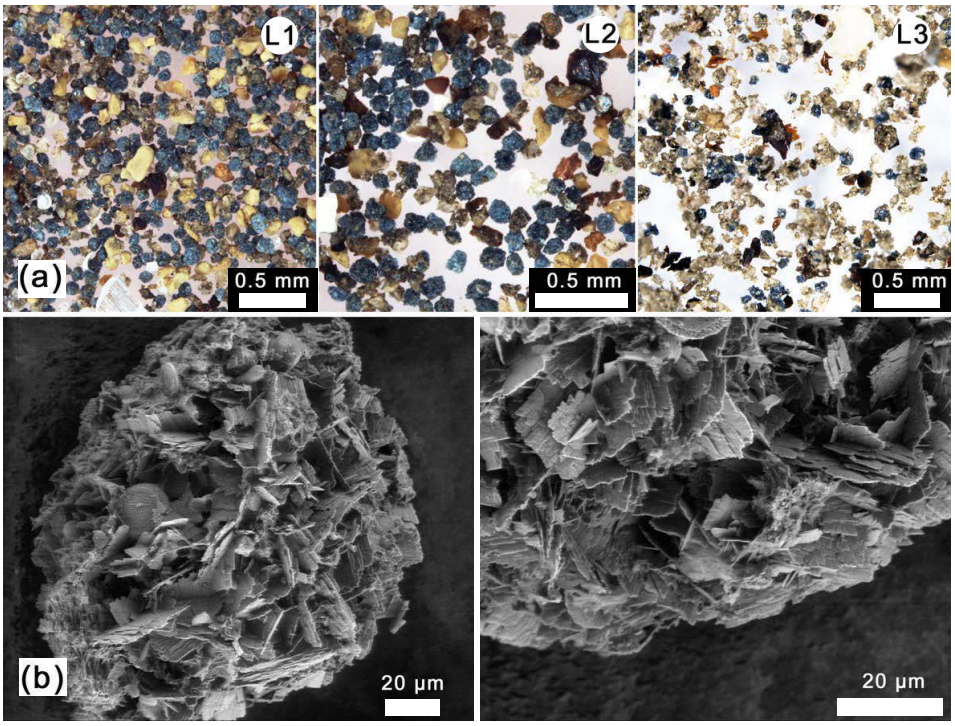

Figure 2.3: (a) Reflected-light microscope images of heavy-liquid separated, high-density, samples from three different sediment depths (L1: 0–10 cm, L2: 11–20 cm, L3: 21–30 cm) of Lake Groß-Glienicke. **(b)** Scanning electron micrographs of dark blue nodules enriched in high-density samples from L1–L3.

but absent from subjacent sediment layers (23–40 cm). The heavy-liquid-separated, high-density sediment samples ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$, from sediment depth layers L1: 0–10 cm, L2: 11–20 cm, and L3: 21–30 cm) were enriched with the dark blue nodules (Fig. 2.3a). Scanning electron micrographs of these blue nodules showed them to be spherical aggregates (40–180 μm in diameter) of platy- and needle-shaped crystals (Fig. 2.3b). Occasionally the aggregates also included organic debris such as diatom shells.

The XRD patterns of high-density samples from sediment layers L1, L2 and L3 showed reflexes characteristic for vivianite, and confirmed the existence of the mineral in the sediment (Fig. 2.4a). The abundance of blue nodules in samples from L1 and L2 was similar to each other but higher than in samples from L3 (Fig. 2.3a). Iron, P and Ca were most abundant of the six elements in the high-density samples from layers L1 and L2; S, Al and Mn were present at much lower concentrations (Table 2.1). In L3, the relative amount of Fe, Ca, and Al did not significantly differ from that in L1 and L2. The relative amount of P of samples from L1 and L2 was similar, whereas the amount in L3 was significantly lower. For S, the relative amount was more than four times higher in samples from L3 than in samples from L1; for Mn, the relative amount in samples from L1 and L2 was similar, whereas L3 had a significantly lower concentration.

Table 2.1: Elemental composition [mol %] of high-density samples ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$) from three different sediment depth layers (L1–L3) of Lake Groß-Glienicke from September 2012 and May 2013. Data are mean ± standard deviation (SD, $n = 5$).

Sediment depth	Fe	Ca	P	S	Al	Mn
L1 (0–10 cm); $n = 5$	43.0 ± 6.3	23.0 ± 11.0	23.5 ± 2.3	3.8 ± 1.5	3.4 ± 1.3	3.3 ± 0.4
L2 (11–20 cm); $n = 5$	51.2 ± 2.3	11.6 ± 2.5	23.0 ± 2.3	6.5 ± 2.1	5.1 ± 1.5	2.8 ± 0.6
L3 (21–30 cm); $n = 5$	55.9 ± 11.4	11.6 ± 4.5	13.9 ± 1.9	18.0 ± 2.5	7.4 ± 3.0	1.7 ± 0.3

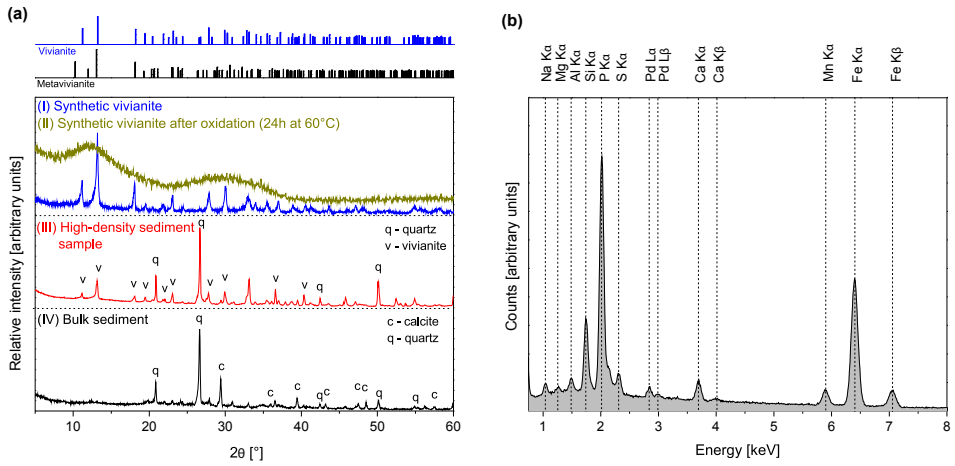

Figure 2.4: (a) XRD patterns of (I) synthetic vivianite, (II) synthetic vivianite after oxidation at 60 °C for 24 h, (III) high-density sample and (IV) bulk sediment. Characteristic reflexes of vivianite could only be observed after heavy-liquid separation in the high-density sample (III). The line patterns of vivianite (blue, file number 96-901-2899) and metavivianite (black, file number 96-100-1784) use data from the Crystallography Open Database (COD) REV 64680 (2012 edition). **(b)** SEM-EDX elemental spectrum obtained from a dark blue sediment concretion from Lake Groß-Glienicke. The corresponding atomic Fe:P ratio is 1.49. Elemental peaks of carbon and oxygen are omitted.

The SEM-EDX analysis on the dark blue aggregates revealed the major elemental constituents to be Fe and P, with a mean Fe:P ratio of 1.49 ± 0.1 (determined from peak area, Fig. 2.3b), which is close to the Fe:P ratio of vivianite (Fe:P = 1.5). The Si content was high, reaching 8 mol%. Minor constituents of aggregates were Mn (4 mol%), Ca (3 mol%), S (2 mol%) as well as Mg and Al (both $\leq$ 1.5 mol%).

Magnetic hysteresis measurements showed that in comparison to bulk sediment, the high-density samples were enriched with paramagnetic material such as vivianite and iron sulfides (FeS_x) (Fig. 2.5a). Both bulk sediment and high-density samples contained ferrimagnetic material, most probably magnetite, recognised by the opening of the hysteresis loops.

The vivianite content ($c_{\text{vivianite}}$ [weight as % of total]) in high-density samples was estimated by comparing the measured paramagnetic mass-specific susceptibility of a high-density sample (MS_{sample} [$m^3\,kg^{-1}$]) with the value

given for vivianite, of $MS_{vivianite} = 1.05 \times 10^{-6}\,m^3\,kg^{-1}$ (Minyuk *et al.*, 2013). The MS_{sample} values were calculated from the slope of the linear increasing part of the hysteresis loops after magnetic saturation of ferrimagnetic minerals. The relative vivianite content in a high-density sample is then given as follows:

$$c_{vivianite} = \frac{MS_{sample}}{MS_{vivianite}} \times 100. \tag{2.1}$$

This calculation is valid assuming that: (1) the contribution of diamagnetic materials, such as calcium carbonate and quartz, to the overall measured magnetic susceptibility is small, and (2) vivianite is the only paramagnetic material present in the high-density samples. Our MS_{sample} values ranged from 1.7×10^{-7} to $3.6 \times 10^{-7}\,m^3\,kg^{-1}$, which is equivalent to a relative vivianite content of 22 to 48 weight as % of total. These values exceeded the maximum vivianite content based upon the amount of P present in the high-density samples (Fig. 2.4b).

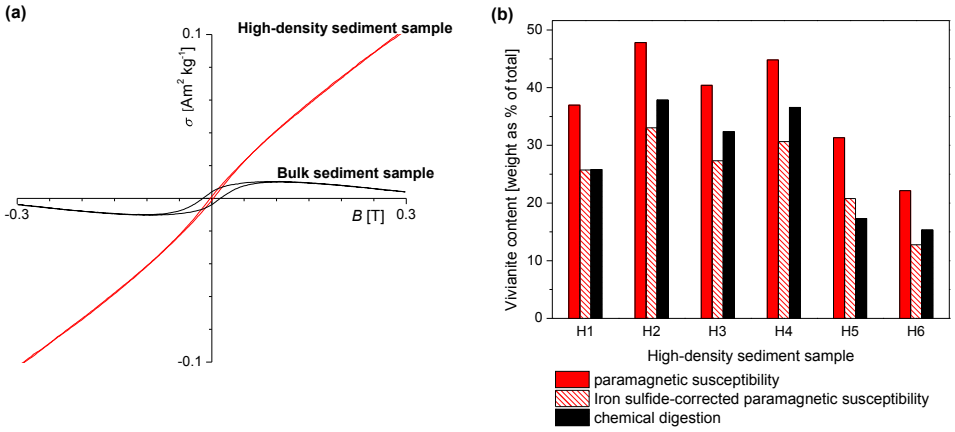

Figure 2.5: (a) Magnetisation σ [$A\,m^2\,kg^{-1}$] vs. magnetic field B [T], peak value $B = 0.3$ T of a high-density sample, and a bulk sediment sample from 10 cm sediment depth. The positive slope of the high-density sample at higher magnetic fields indicates enrichment with paramagnetic material after heavy-liquid separation. **(b)** Variations in vivianite content (expressed as % weight of the sample) in each of six high-density samples, based upon paramagnetic susceptibility, iron sulfide-corrected paramagnetic susceptibility and chemical digestion.

To correct MS_{sample} for the contribution of paramagnetic FeS_x, we assumed all sulfur (Table 2.1) to be present as FeS in the high-density samples. Accordingly, high-density samples contained between 4 and 21 weight as % of total FeS. Assuming a paramagnetic mass specific susceptibility of FeS, of $MS_{FeS} = 1.54 \times 10^{-7}\,m^3\,kg^{-1}$ (Lide, 2004), equation (1) can be re-written as follows:

$$\begin{aligned} c_{vivianite} &= \frac{(MS_{sample} - MS_{sample,\,FeS})}{MS_{vivianite}} \times 100 \\ &= \frac{(MS_{sample} - (MS_{FeS} \times c_{FeS}))}{MS_{vivianite}} \times 100, \end{aligned} \tag{2.2}$$

where $MS_{sample,\,FeS}$ $[m^3\,kg^{-1}]$ is the contribution of paramagnetic FeS to the measured mass-specific susceptibility and c_{FeS} is the content of FeS [weight as % of total] in a high-density sample. The FeS-corrected vivianite content in high-density samples ranged between 13 and 33 weight as % of total. These values were, except for sample H5, 1 to 15 % lower than the vivianite content derived from chemical digestion (Fig. 2.5b).

Relating the vivianite content in the high-density samples, calculated from chemical digestion, to the equivalent amount in bulk sediment, we were able to assess the significance of vivianite formation for the retention of P in the sediment. In samples from L1 and L2, vivianite formation accounted for 0.95 $\pm$ 0.21 mg g^{-1} dry weight P and 0.96 $\pm$ 0.16 mg g^{-1} dry weight P, respectively (Fig. 2.6a). The vivianite accounts for 20 % of TP concentration in the upper 20 cm of the sediment. In contrast, there was significantly less P in the high-density samples from L3 (0.54 $\pm$ 0.13 mg g^{-1} dry weight P). This lower concentration is because depth layer L3 included sediment layers where no vivianite nodules were present (24–30 cm sediment depth).

The vivianite–nonvivianite transition at a sediment depth of 23 cm coincided with a peak in sedimentary Fe and P content (Fe 80 mg g^{-1} dry weight, P 5 mg g^{-1} dry weight) (Fig. 2.6a and b). Above this, in the upper 23 cm of the sediment, the Fe (and P) content was on average 2.4 (and 3.1) times higher than in the deeper, nonvivianite-bearing sediment zone (24–30 cm sediment depth). The course of manganese resembled that of Fe but showed an

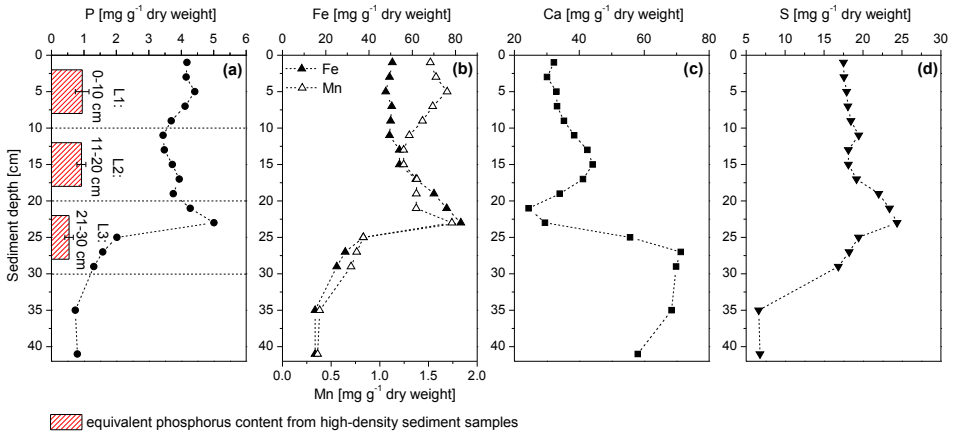

Figure 2.6: Sediment stratigraphic chart of **(a)** phosphorus (P), **(b)** iron (Fe) and manganese (Mn), **(c)** calcium (Ca) and **(d)** sulfur (S) of Lake Groß-Glienicke from May 2013. Bar charts in graph **(a)** represent the equivalent P content analysed in the high-density samples from depth layers L1, L2 and L3. Error bars denote ± SD, $n = 5$.

increasing trend above 12 cm sediment depth (Fig. 2.6b). Calcium content showed a reverse trend, and decreased on average by a factor of 1.9 in the vivianite-bearing sediment zone compared to the nonvivianite zone (Fig. 2.6c). The mean molar Fe:S ratio increased from 0.9 in the 25–30 cm sediment depth, to 1.6 in the upper 23 cm of vivianite bearing sediment (Fig. 2.6b and d).

2.5 Discussion

2.5.1 Identification and quantification of vivianite

The heavy-liquid separation and the enrichment of vivianite aggregates are crucial steps for the direct identification of vivianite by X-ray diffraction. In our study, X-ray diffraction was successful, even though the vivianite nodules were partially oxidised due to contact with air (Figs. 2.3a and 2.4a) and already are an alteration product of unoxidised, pristine vivianite. The diffraction pattern of synthetic vivianite powder, both in its slightly oxidised form (blue appearance) and after heating at 60 °C for 24 h supported that the vivianite nodules detected in the sediment were slightly surface-oxidised only

and did not lose their characteristic diffraction pattern upon freeze-drying and exposure to air. Comparing the diffraction pattern of the high-density sample with the reference diffraction pattern of vivianite and metavivianite (which accounts for a partial oxidation of Fe(II)) there was even a higher conformity with the vivianite reference pattern than with the metavivianite reference pattern (Fig. 2.4a). This finding confirms that an aerobic handling of sediment does not lead to a significant oxidation of vivianite and the mineral is detectable by X-ray diffraction even after contact with air; this is contrary to what has been reported by Olsson *et al.* (1997) and März *et al.* (2008). According to these studies, vivianite is not expected to be detectable by X-ray diffraction after contact with air due to its high sensitivity towards oxidation. Aerobic handling of sediment and freeze-drying, however, might have impacted the speciation of sulfur – i.e. crystalline FeS_2 and FeS might have been oxidised and altered to amorphous phases (Hjorth, 2004).

EDX analysis and scanning electron microscopy reveal fundamental characteristics of the mineral aggregates, and a conventional reflected-light microscope allows identification of single vivianite nodules out of bulk sediments. Thus, a combination of techniques allowed a qualitative investigation of vivianite deposits in different sediment layers and comparison with results from saturation calculations. The enrichment of high-density samples with vivianite nodules further allowed us to assess the amount of vivianite present in the sediment. To estimate the quantity of vivianite in high-density sediment samples, the vivianite content was calculated based upon two different methods: (1) chemical digestion, and (2) magnetic hysteresis measurements. The latter method provides a different, and independent approach to estimate the vivianite content, taking advantage of the heavy-liquid separation of sediment samples and the paramagnetic nature of vivianite.

2.5.2 Contribution of vivianite to phosphorus retention

The presence of vivianite within the first centimetre of the lacustrine sediment of freshwater Lake Groß-Glienicke shows that vivianite is currently forming. The incorporation of diatom shells and other organic debris within

the nodules confirms their authigenic origin (Fig. 2.3b). The occurrence of vivianite nodules in a recent and unlayered sediment horizon distinguishes the vivianite finding described here from Lake Groß-Glienicke from the vivianite deposits regularly detected in palaeolimnetic core records (e.g. Brauer *et al.*, 1999; Sapota *et al.*, 2006; Minyuk *et al.*, 2013).

In the high-density samples from layers L1 (0–10 cm) and L2 (11–20 cm) there was a higher amount of vivianite nodules than in samples from layer L3 (21–30 cm). These observations are reflected in the P content of the high-density sediment samples. In samples from L1 and L2 the P content was similar (to each other), whereas samples from L3 contained significantly less P.

Due to the high enrichment of vivianite nodules in the high-density samples, the P content that we determined mainly represented the amount of P bound in vivianite. We cannot exclude that part of the P analysed in the high-density samples originated from compounds other than vivianite, such as P sorbed onto the surface of Fe(III) minerals which resisted reductive dissolution, Ca-associated P, or other Fe-phosphates. These compounds were expected to accumulate in the high-density samples as their density is higher than $2.3\,\mathrm{g\,cm^{-3}}$ and chemical digestion data confirmed the presence of Ca and high content of Fe in these samples (Table 2.1). However, our results from magnetic susceptibility measurements support the assumption that the amount of P analysed in the high-density samples could mainly be attributed to vivianite-bound P.

Provided that the weakening of the measured positive magnetisation due to the presence of diamagnetic Si and Ca compounds is small, the vivianite content can be determined from paramagnetic susceptibility. This assumption is valid, since the values of the diamagnetic mass-specific susceptibility of SiO_2 and $CaCO_3$ are more than two orders of magnitude smaller than that of vivianite (Lide, 2004). Even if high-density samples contained 3–5 times more diamagnetic SiO_2 and $CaCO_3$ than vivianite, the correspondent weakening of the positive magnetisation was negligible. The contribution of paramagnetic FeS_x to the measured positive magnetisation of high-density samples was significant (Fig. 2.5b) when assuming all sulfur to be present as FeS. For the

susceptibility correction we used the MS_{FeS} value given by Lide (2004). The FeS correction could account for the overestimation of the vivianite content derived from uncorrected magnetic susceptibility data. The FeS-corrected vivianite contents were, except for one sample, lower than values derived from chemical digestion. However, it is important to note that the relative changes in vivianite content between different high-density samples were determined similarly by both the chemical digestion and the FeS-corrected paramagnetic susceptibility methods (Fig. 2.5). Considering the range of a factor of two for the mass-specific magnetic susceptibility of vivianite (Minyuk *et al.*, 2013), the vivianite contents determined by both the chemical digestion and the FeS-corrected paramagnetic susceptibility methods match acceptably.

Furthermore, a high-density sediment sample from 35 cm sediment depth (data not shown), containing no vivianite nodules, demonstrated a negative susceptibility at higher magnetic fields, indicative of a majority of diamagnetic material present in the high-density sediment sample. The P content of this sample accounted only for $0.05\,mg\,g^{-1}$ dry weight P which is less than 6 % of the P content detected in high-density samples from L1 and L2. The good agreement between results from magnetic susceptibility measurements and chemical digestion confirmed that the amount of P analysed in the high-density samples in sediment layers L1–L3 mainly represented vivianite-bound P.

Although the sediment preparation method we used neglected vivianite nodules smaller than 80 μm in diameter, the amount of vivianite present in the high-density samples serves as a reliable proxy for the overall vivianite content in the sediment. The sieving step was applied in order to maximise the enrichment of vivianite nodules in high-density samples and minimise the relative amount of small-sized ($< 80\,\mu m$) Si and Ca compounds at the same time.

Our results suggest a homogeneous vivianite content in the upper 20 cm of the sediment. Vivianite formation significantly contributed to P retention in Lake Groß-Glienicke, accounting for 20 % of the total sedimentary P in the upper 20 cm of the sediment (Fig. 2.6). Assuming an increase in total sedimentary P due to the artificial application of Fe during lake restoration of

$2.5\,mg\,g^{-1}$ in the upper 20 cm of the sediment in comparison to sediment layers deposited prior to the in-lake measure, vivianite formation could explain about 40 % of this increase. The remaining 60 % of increase in total sedimentary P might be due to Fe(III)-phases which sorb P, and mixed Fe(III)/Fe(II) phosphate minerals, which resisted reductive dissolution within the anoxic sediment matrix (Hyacinthe & Van Cappellen, 2004; Lehtoranta *et al.*, 2009). Redox-sensitive Fe(III)-phases could be preserved by a protective coating of FeS_x preventing further reduction (De Vitre *et al.*, 1988). Moreover, P originating from preserved organic material, which co-precipitated during iron oxidation, could significantly contribute to the increase in P burial after the addition of Fe during lake restoration (Lalonde *et al.*, 2012). The presence of these compounds may explain the peak in P and Fe content at the sediment depth of 23 cm, even though no elevated vivianite contents could be detected at this depth.

2.5.3 Prediction of vivianite formation by saturation calculations

Changes in pH and dissolved substances across the SWI (Fig. 2.1) are due to the deposition of organic and inorganic matter, and its subsequent microbial decomposition. Along with the liberation of SRP and Fe^{2+} there was moderate vivianite supersaturation (SI = 3–4) throughout the upper 30 cm of the sediment (Fig. 2.1). The decrease in orthophosphate activity with sediment depth is due to the declining pH counteracting the concomitant increase of SRP concentration with depth. While the activity of H^+ and SRP varied by a similar factor, the variation in pH has a stronger influence on the saturation state of vivianite than does the change in SRP concentration. Since simultaneous with the decrease in orthophosphate activity, the activity of Fe^{2+} increased with depth, the degree of vivianite supersaturation persisted. The degree of supersaturation underlines that mineral formation is slow, and not governed by the saturation state of the pore water but rather by another process, as proposed by Postma (1981) and Emerson & Widmer (1978). According to those studies crystal growth is driven by surface reactions and is not diffusion controlled. Formation of siderite ($FeCO_3$) which potentially

competes with vivianite for Fe^{2+} is supposed to be controlled by very slow precipitation kinetics (Postma, 1981). Therefore, it is unlikely that the near-equilibrium conditions we report for Lake Groß-Glienicke indicate siderite precipitation. No crystalline siderite could be identified in the high-density samples using the XRD pattern.

According to these saturation calculations, and from a thermodynamic point of view, the precipitation of vivianite was favoured in the upper 30 cm of the sediment. The present geochemical conditions, with relatively high Fe^{2+} concentrations (0.02 to 0.2 mmol L^{-1}) and high SRP concentrations (0.04 to 0.09 mmol L^{-1}), at neutral to slightly alkaline pH in the absence of free sulfides, plot within the stability field of vivianite proposed by Nriagu (1972) and Nriagu & Dell (1974). However, to rely upon these calculations to predict in situ vivianite formation omits consideration of a key feature, namely the sharp transition between the vivianite-bearing and nonvivianite-bearing sediment layers. Vivianite was only present in the upper 23 cm of the sediment, not in subjacent sediment layers even though the pore water was supersaturated at sediment depths of 24 and 28 cm. Assuming constant precipitation of vivianite from supersaturated pore water, the highest concentrations of vivianite should be in sediment layers which have been supersaturated the longest time, for example in the sediment deposited shortly after the iron addition. However, this was not the case for Lake Groß-Glienicke. From our findings, it is therefore questionable whether supersaturated pore water alone is a reliable predictor of the in situ formation of vivianite.

2.5.4 Processes influencing vivianite formation

We consider that the Fe application in 1992/93 was the stimulus for vivianite formation in Lake Groß-Glienicke. In 2003 Gächter & Müller (2003) used a simple conceptual model to explain that an increasing ratio of reactive Fe(II) to reactive P leads to an increased permanent P burial through the formation of a solid ferrous iron phosphate, such as vivianite. It is exactly that shift in geochemical conditions which led to the favourable conditions for vivianite formation in Lake Groß-Glienicke. During restoration of Lake

Groß-Glienicke Fe was provided in surplus. As a consequence, not all reactive Fe(II) is precipitated as solid FeS_x but can react with PO_4^{3-} to form stable Fe(II)-phosphate minerals (Gächter & Müller, 2003; Kleeberg *et al.*, 2013). The relative S content in the sediment decreased after the artificial application of iron and explains why high-density samples from L1 and L2 contained less S than samples from L3 (Table 2.1).

The Fe and Mn content is elevated throughout the upper 23 cm of the sediment (Fig. 2.6), because there has been a continuous cycling of both elements between their dissolved and particulate forms at the SWI after the Fe application. This feature reflects the change in redox conditions in the hypolimnion and at the SWI after the Fe supplement, i.e. the sediment surface has become more oxidised. A high reactive Fe(II) concentration led in turn to the formation of vivianite in freshly deposited sediments after the Fe application. The layer of formation of vivianite is the uppermost sediment horizon close to the SWI. This explains the homogeneous vivianite content in the upper 20 cm of the sediment, and emphasises that supersaturated pore water alone is not sufficient to cause vivianite formation.

At the SWI, fresh organic matter is decomposed, and iron(oxy)hydroxides undergo reductive dissolution, leading to the release of Fe^{2+}, SRP from organic matter, and the liberation of previously adsorbed PO_4^{3-} from iron(oxy)hydroxides. The presence of vivianite aggregates in association with organic matter or organic-rich deposits has been reported by numerous authors (Mackereth, 1966; Kjensmo, 1968; Rosenqvist, 1970; Postma, 1981; Peretyazhko & Sposito, 2005; Taylor *et al.*, 2008), suggesting a crucial function of this organic material for the formation of crystal aggregates. The gel-like pore structure of a sediment matrix rich in organic matter, in combination with an intensified release of SRP and Fe^{2+} due to microbial activity, may serve as necessary prerequisite for vivianite formation in sediments. Through the activity of bacteria, cell-mediated microenvironments within the sediment matrix may evolve, sustaining vivianite-supersaturation during crystal growth, even on a small scale (Cosmidis *et al.*, 2014). Hydrophic, negatively charged, carbon-rich fibres which build up a structure of walls within the sediment may thereby catalyse the growth of seed crystals (Zelibor *et al.*, 1988).

2.6 Conclusions

Heavy-liquid separation of sediment leads to an enrichment of vivianite nodules in high-density samples, and is key to demonstrating the presence of vivianite by X-ray diffraction. The enrichment achieved after sediment preparation, and combination of the results from standard chemical digestion and magnetic hysteresis measurements, allow quantification of the P bound in vivianite for different sediment depths. However, the absence of vivianite from layers of sediment that are supersaturated with pore water constrains the validity of equilibrium calculations regarding the in situ precipitation and occurrence of vivianite. At our study site at Lake Groß-Glienicke, formation of vivianite was triggered by an artificial Fe supplement, and explains 20 % of total P in sediment layers deposited after the in-lake measure. Our results emphasise the role of Fe, and the formation of vivianite in particular, in the long-term retention of P in the sediment, which enabled the system to recover from its former eutrophic state to its current mesotrophic level.

Chapter 3

Sedimentary sulphur:iron ratio indicates vivianite occurrence: a study from two contrasting freshwater systems

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3.1 Abstract

An increasing number of studies constrain the importance of iron for the long-term retention of phosphorus (P) under anoxic conditions, i.e. the formation of reduced iron phosphate minerals such as vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$). Much remains unknown about vivianite formation, the factors controlling its occurrence, and its relevance for P burial during early sediment diagenesis. To study the occurrence of vivianite and to assess its relevance for P binding, surface sediments of two hydrologically contrasting waters were analysed by heavy-liquid separation and subsequent powder X-ray diffraction. In Lake Arendsee, vivianite was present in deeper sediment horizons and not in the uppermost layers with a sharp transition between vivianite and non-vivianite bearing layers. In contrast, in lowland river Lower Havel vivianite was present in the upper sediment layers and not in deeper horizons with a gradual transition between non-vivianite and vivianite bearing layers. In both waters, vivianite occurrence was accompanied by the presence of pyrite (FeS_2). Vivianite formation was favoured by an elevated iron availability through a lower degree of sulphidization and was present at a molar ratio of total sulphur to reactive iron smaller than 1.1, only. A longer lasting burden of sediments by organic matter, i.e. due to eutrophication, favours the release of sulphides, and the formation of insoluble iron sulphides leading to a lack of available iron and to less or no vivianite formation. This weakening in sedimentary P retention, representing a negative feedback mechanism (P release) in terms of water quality, could be partly compensated by harmless Fe amendments.

3.2 Introduction

Phosphorus (P) is one of the key nutrients in aquatic systems and often governs their primary production. Although in many European countries nutrient inputs have been significantly reduced within the last 30 yr, the eutrophication of rivers, lakes and coastal seas is still an issue (Smith *et al.*, 2006; Withers *et al.*, 2014). Ultimately, it is the balance between sources and sinks which determines P availability for primary producers in aquatic

ecosystems. Besides fluvial and groundwater P export, the burial in sediments accounts for the major loss of P in aquatic ecosystems.

The sequestration of P in sediments is the result of multiple chemical reactions which are driven by the mineralisation of organic matter (OM) through microorganisms. Along with these reactions the elemental cycles of iron (Fe) and sulphur (S) play a crucial role in binding of P in sediments. Einsele (Einsele, 1936) and Mortimer (Mortimer, 1941) revealed the tight coupling between the Fe and the P cycle since iron(oxyhydr)oxides act as efficient sorption agents for orthophosphate (PO_4^{3-}). By this mechanism PO_4^{3-} is trapped and surface sediments can act as a barrier for upward diffusing PO_4^{3-} as long as the overlying water is oxic (Hupfer & Lewandowski, 2008). Under anoxic conditions, however, reduction of iron(oxyhydr)oxides may result in the release of PO_4^{3-} into the water column. Due to this redox sensitivity, P associated with Fe has long been considered not to be a significant burial form in the long-term.

The cycling of S is closely coupled to the transformations of P and Fe. Since free sulphides (S^{2-}) react with ferrous Fe (Fe(II)) to form insoluble Fe sulphides (FeS_x), the decomposition of OM by sulphate reducing microorganisms depletes the reactive Fe pool (this includes iron(oxyhydr)oxides and dissolved ferrous Fe) in the sediment and counteracts the functioning of Fe in binding P. Simultaneously, iron(oxyhydr)oxide-P compounds may undergo reductive dissolution in the presence of S^{2-} which leads to increased PO_4^{3-} concentrations in the water (Smolders & Roelofs, 1993; Murray, 1995; Roden & Edmonds, 1997; Zak *et al.*, 2006). This reductive phosphate release can also trigger authigenic P mineral formation, in particular reduced Fe phosphates if not all reactive Fe is precipitated by S^{2-}. Therefore, the extent of S^{2-} production and the amount of reactive Fe available crucially determines the effectivity of Fe in binding P, significantly influencing P retention in the short- and also in the long-term (Gächter & Müller, 2003; Kleeberg *et al.*, 2013).

Recent studies from fresh- and marine water bodies prove Fe-P compounds to be of significance for P burial in anoxic sediments and suggest that this is due to the formation of stable reduced Fe phosphate minerals (März *et al.*,

2008; Lehtoranta *et al.*, 2009; Jilbert & Slomp, 2013; Slomp *et al.*, 2013; Cosmidis *et al.*, 2014; Dijkstra *et al.*, 2014; Hsu *et al.*, 2014; Rothe *et al.*, 2014). However, the determination of the exact binding form(s) is difficult, and the mechanisms leading to lasting Fe-associated P burial under anoxic conditions are not fully understood.

Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) is the most common reduced Fe(II)-phosphate mineral forming under anoxic, non-sulphidic conditions in Fe- and organic-rich soils and sediments (Nriagu, 1972; Berner, 1981b; Roden & Edmonds, 1997). The occurrence of vivianite in sediments has been proposed by many authors, however, the direct identification is difficult. There is limited knowledge about its formation conditions and its relevance for P retention in surface sediments. Only recently, we applied a novel approach which enabled us to identify vivianite by X-ray diffraction and showed vivianite to be a significant burial form in a lake sediment artificially enriched in Fe (Rothe *et al.*, 2014).

To investigate the relevance of Fe-associated P burial through the formation of reduced Fe(II)-phosphate minerals, we analysed surface sediments of two contrasting eutrophic freshwater systems, i.e. a deep lake that is poor in Fe (Lake Arendsee), and a shallow lowland river rich in Fe (Lower Havel). In particular, our study aims for a better understanding under which sedimentary conditions vivianite occurs and how the cycling of Fe, P and S affects the formation of vivianite. For these purposes, surface sediments were separated by a heavy-liquid to identify vivianite by X-ray diffraction. Furthermore, sediments were characterised by elemental analysis, P fractionation, total inorganic S extraction and radioisotopic dating.

3.3 Materials and methods

3.3.1 Study sites and sample collection

Lake Arendsee is a dimictic, eutrophic karst lake ($z_{max} = 48\,m$, $z_{mean} = 29\,m$, $A = 5.13\,km^2$) located in northern Germany (52°53′21″ N, 11°28′27″ E). It has a long water residence time (50-60 yr, (Meinikmann *et al.*, 2015)). During summer stratification (April-December) the hypolimnion becomes increasingly

anoxic and S^{2-} is present from August to December. The surface sediment has a low Fe content and is rich in Ca and OM (5-15 cm: Fe 3 mg g^{-1} dry weight, [henceforth denoted as mg gdw^{-1}] and OM 20 % dry weight, [henceforth denoted as % dw]). However, Fe content drastically increases below $\approx$ 23 cm sediment depth (Findlay *et al.*, 1998). In the past, there were several attemps to reduce the P concentration of the lake water, at last in 1995, when calcareous mud from the littoral zone of the lake was used for capping the sediment (Hupfer *et al.*, 2000). Today, this Ca-rich layer is located in 12-15 cm sediment depth.

The Lower Havel is a polymictic lowland river located west of Berlin, Germany (52°27′06″ N, 13°09′29″ E). The river comprises of lake-like widenings and is contrasting in its hydrological and biogeochemical conditions in comparison to Lake Arendsee. It stretches about 11 km and water depth varies between 4 m and 8 m with a maximum of 11 m. The hydraulic residence time is on average 19 d (2000-2009) (Grüneberg *et al.*, 2015). Most of the time of the year, the water column is well oxygenated, however, oxygen depleted conditions in bottom waters may occur occassionally in summer during periods of low winds and high temperatures. The sediments are organic-rich and have a mud-like texture. The depth of oxygen penetration into the sediment is therefore considered to range a few millimetres only. The sediment is non-sulphidic and the Fe content in the upper sediment is about 10 times higher than in Lake Arendsee.

Undisturbed sediment cores (60 mm and 96 mm in diameter, 30-50 cm long) were collected by a gravity corer (UWITEC) at the deepest site in Lake Arendsee and at 8 m water depth in Lower Havel and sectioned into 10 mm or 20 mm slices. For Lake Arendsee sediment cores were collected in June 2007 for sequential P extraction, in February 2014 for the analysis of vivianite deposits (heavy-liquid separation) and elemental analysis, and in October 2014 for total reducible inorganic S (TRIS) extraction and radioisotopic dating. For Lower Havel, sediment cores were taken in October 2011 for sequential P extraction, in May 2012 for TRIS extraction, in October 2013 for the analysis of vivianite deposits (heavy-liquid separation) and elemental analysis, and in October 2014 for radioisotopic dating.

For all sampling of sediments no specific permission was required. The sampling sites did not involve private or protected areas. The research activities were carried out in cooporation with the relevant regulatory body (Senate of Berlin, and State Agency for Flood Protection and Water Management Saxony-Anhalt (LHW)).

3.3.2 Analysis

Radioisotopic dating

Fresh sediment was freeze-dried in a vertical resolution of 1 cm. Samples were sealed with a gas tight foil and stored for one month in order to receive secular equilibrium between ^{222}Rn and its short lived daughter isotopes. The γ-spectrometric measurements of ^{210}Pb, ^{226}Ra, ^{214}Bi, ^{137}Cs, ^{40}K and ^{7}Be were carried out using a n-type coaxial Ge detector (CANBERRA). Supported ^{210}Pb activities were calculated assuming secular equilibrium between ^{226}Ra and ^{210}Pb. The constant rate of supply (CRS) model (Appleby & Oldfield, 1978) and the constant flux and constant sedimentation model (CF-CS) (Robbins, 1978) for ^{210}Pb were used to construct a sediment chronology.

Chemical analysis

Freeze-dried subsamples of sediment (in the following text referred to as "bulk" sediment) were homogenised in an agate mortar and analysed for total metal concentrations after wet digestion (HCl 36 %, HNO_3 76 %, volumetric ratio 1 : 3) in a high-pressure microwave oven (Gigatherm). Concentrations of Al, Ca, Fe, Mn, Mg, and S were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7000series, Thermo Scientific). The acid extractable Fe, henceforth denoted as "Fe", represents an upper limit of all reactive Fe phases present in the sediment and does not include Fe bound in silicates which is non-reactive in early diagenesis.

Content of OM was determined as loss on ignition (LOI, 6 h, 450 °C). Total P (TP) was determined photometrically by the molybdenum-blue method (Murphy & Riley, 1962) after sediment combustion (2 h, 550 °C) and hot digestion (100 °C, 2 M HCl) (Andersen, 1976).

Sedimentary P forms of fresh sediment were characterised by a sequential extraction according to (Psenner *et al.*, 1984) with slight modifications (Hupfer *et al.*, 1995). The extraction separates six different P forms: (1) loosely adsorbed P, immediately available P (NH_4Cl-TP), (2) redox sensitive P, mainly bound to Fe-(hydr)oxides (BD-TP), (3) metal-bound P, mainly associated with Fe- and Al-oxides (NaOH-SRP), (4) organic-bound P (NaOH-NRP), (5) P bound in calcium carbonates and apatite (HCl-TP), and (6) residual P determined after digestion of remaining sediment (Res-P). Synthetic, surface-oxidised vivianite powder (Dr. Paul Lohmann GmbH KG) with a blue appearance (Rothe *et al.*, 2014) and a high-density sample containing naturally born vivianite were also sequentially extracted by schemes of Psenner *et al.* (1984) and Ruttenberg (1992). Following the SEDEX scheme Ruttenberg (1992), the first two extraction steps were carried out representing loosely adsorbed P (Ex-P, step I), and iron(oxyhydr)oxide-bound P and vivianite (CDB-P, step II).

From fresh sediment samples three inorganic S fractions were determined by sequential extraction (Canfield *et al.*, 1986): (1) acid volatile S (AVS), considered to represent Fe monosulphides (mackinawite, troilite and pyrrhotite), (2) chromium reducible S (CRS), attributed to disulphidic S forms (pyrite, marcasite) and (3) elemental S (S^0) (Morse *et al.*, 1987). Sulphide concentration in sediment extracts was determined by polarography (Metrohm). Total S content was determined with a CN analyser (Vario EL). Organic S (S_{org}) was then calculated as total S - (AVS + CRS + S^0). Total Fe content was determined by ICP-OES after wet digestion of dry sediment as described above. The relative contribution of mono- and disulphidic-bound Fe on total Fe was then calculated according to stoichiometry and the S^{2-} concentration analysed in the AVS and CRS extracts. All determinations were performed in duplicate.

Heavy-liquid separation of sediment

Fresh sediment samples were freeze-dried and a heavy-liquid separation was applied (Rothe *et al.*, 2014) in vertical resolution of 2 cm. A sodium polytung-

state solution ($3\,Na_2WO_4 \cdot 9WO_3 \cdot H_2O$, ABCR Co.) was used to separate the sediment into a low-density ($\rho \leq 2.3\,g\,cm^{-3}$) and a high-density ($\rho > 2.3\,g\,cm^{-3}$) sample. Deviating from the procedure described in Rothe *et al.* (2014), sediment samples were not sieved prior to the heavy-liquid separation.

High-density samples were analysed for the presence of vivianite, appearing as dark blue sediment concretions using a reflected-light microscope. Mineral composition of high-density samples and bulk sediment samples was characterized by powder X-ray diffraction (XRD) with a Bruker AXS D8 diffractometer equipped with Cu-K_α-radiation and a Sol-X solid state detector. The XRD-pattern were measured between 5 and 60 ° 2θ with a step of 0.05 ° 2θ and an integration time of 9 s. Scanning electron micrographs of sediment concretions were obtained with a FEI Quanta 600FEG field emission environmental scanning electron microscope (FE-ESEM).

To get a rough estimate of the magnitude of vivianite-P to sedimentary TP in relation to other P binding partners, concentrations of Al, Ca, Fe, Mn, Mg and P were analysed in the high-density samples by ICP-OES as described above. The share of vivianite-P to sedimentary TP was calculated using the dry mass and the P content of the high-density sample and comparing it with the original sample mass and the P content prior to heavy-liquid separation (Rothe *et al.*, 2014).

3.4 Results

3.4.1 Vertical distribution of elements and phosphorus fractions

For Lake Arendsee and Lower Havel elemental analysis of sediment revealed contrasting trends in the content of sedimentary TP with depth (Fig. 3.1a, d). Whereas in sediments of Lake Arendsee TP content was low in the upper 25 cm of the sediment (TP: 0.3-1.2 $mg\,gdw^{-1}$) and strongly increased further down-core, in sediments of Lower Havel a contrasting trend was evident. Here, the highest TP content was found in the upper 10 cm of the sediment (4.5-4.7 $mg\,gdw^{-1}$). Further down-core, values decreased by 60 % to be as low as 1.7 $mg\,gdw^{-1}$ in 15 cm depth and were constant to the bottom of the core

(27 cm).

For sediments of Lake Arendsee, the depth profile of Fe (reactive, non-silicate Fe) was similar to that of the TP content (Fig. 3.1a). Iron content was low in the upper 25 cm but strongly increased further down-core to be as high as 53 mg gdw^{-1} at 31 cm depth and was constant down to the bottom of the core. For S, there was a peak at 19 cm depth with values to be as high as 25 mg gdw^{-1}. The molar ratio of total S to reactive Fe (henceforth denoted as "S:Fe") showed an opposing vertical trend to that of TP and Fe: in the upper 25 cm the ratio was as high as 2.5 but decreased further down-core to reach values lower than 0.5 (Fig. 3.1b). For Ca and OM content there were large variations in the upper 25 cm of the sediment (Fig. 3.1c). Further down-core, variations were smaller, and Ca averaged to 89 ± 28 mg gdw^{-1} and, OM to 19 ± 2 % dw.

For Lower Havel, the depth profile of Fe did not show a decreasing trend as observed for TP. Similar to the content of Ca and OM, Fe content was constant in the upper 27 cm and averaged to 48 ± 4 mg gdw^{-1} (Fig. 3.1d, f). The S content increased by more than 300 % down-core, with the lowest and highest value to be in the uppermost and lowermost sediment layer (16 mg gdw^{-1} and 56 mg gdw^{-1}, respectively). The strongest gradient was between 11-15 cm. Accordingly, the molar S:Fe ratio increased down-core. This ratio was as low as 0.6 at 5 cm depth and increased to values higher than 1.5 below 17 cm depth (Fig. 3.1e).

Radioisotopic dating of Lake Arendsee revealed a heterogeneous core. Based upon independent time markers, as there was the artificial layer of calcareous mud corresponding to the year 1995, the Chernobyl accident in 1986 and the nuclear weapon tests in the 1960's, the bottom of the core corresponded to a time prior to 1918 (Fig. 3.1c).

Radioisotopic dating of Lower Havel sediment revealed a homogeneous chronology: the upper 30 cm corresponded to a time span of 22.5 ± 2.5 yr and an avarage dry mass sedimentation rate of 0.144 ± 0.03 g cm^{-2} yr^{-1}. Accordingly, an increasing depth represented an increasing age: 5 cm 3.4 ± 0.4 yr, 10 cm 8.5 ± 0.8 yr, 15 cm 10.7 ± 0.8 yr, 20 cm 14.4 ± 0.9 yr, and 25 cm 18.7 ± 2.0 yr (Fig. 3.1f).

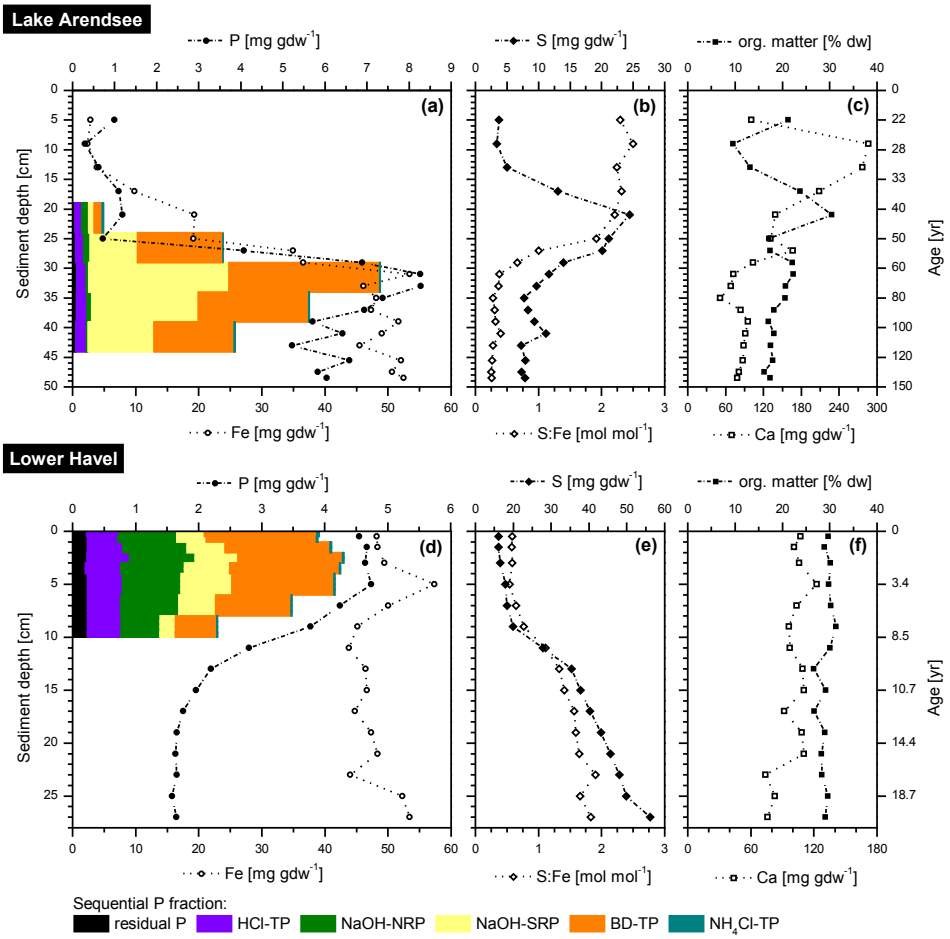

Figure 3.1: Sediment stratigraphic charts of **(a, d)** phosphorus (P) and iron (Fe), **(b, e)** molar ratio of total sulphur to reactive iron (S:Fe) and sulphur (S), and **(c, f)** organic matter (org. matter) and calcium (Ca) from February 2014 (Lake Arendsee) and October 2013 (Lower Havel). According to sediment depth the age of the core is indicated. Bar charts in graph **(a)** and **(d)** indicate six different P forms in the correspondent sediment depth layers: (1) NH_4Cl-TP: loosely adsorbed P, immediately available P, (2) BD-TP: redox sensitive P, mainly bound to Fe-(hydr)oxides, (3) NaOH-SRP: metal P, mainly bound to Fe- and Al-oxides, (4) NaOH-NRP: organic-bound P, (5) HCl-TP: P bound in calcium carbonates and apatite, and (6) Res-P: residual P determined after digestion of remaining sediment. P fractionation data originate from sediment cores taken in June 2007 (Lake Arendsee) and October 2011 (Lower Havel).

P fractionation data from both waters revealed that elevated TP content (Lake Arendsee: 25-44 cm, Lower Havel: 0-10 cm sediment depth) was due to increased burial of two P forms: redox sensitive, Fe-bound P (BD-TP) and metal-bound P (NaOH-SRP) (Fig. 3.1a, d). For Lake Arendsee, these two P forms accounted for 80-95 % of TP between 25-44 cm sediment depth but for less than 45 % between 19-25 cm sediment depth. For Lower Havel, the relative contribution of BD-TP and NaOH-SRP was 40-60 % of TP in the upper 10 cm of the sediment and decreased between 6 cm and 10 cm depth.

3.4.2 Total reducible inorganic sulphur (TRIS)

In Lake Arendsee, there was a S peak in 19 cm depth (Fig. 3.1b). In the core used for TRIS analysis this S peak was 10 cm further down-core than evident from Fig. 3.1b. Accordingly, the highest S content was at 29 cm sediment depth, here (Fig. 3.2a). The stratigraphy of OM and Fe had similar vertical shifts among all cores taken.

The peak in S was due to elevated content of mono- and disulphidic bound S as well as S^0 (Fig. 3.2a). The content of S^0 was 10 times higher above than below the S peak. Assuming all acid volatile S (AVS) to be present as FeS and all chromium reducible S (CRS) to be present as FeS_2, the percentage of sulphidic-bound Fe on total Fe (degree of sulphidization) varied between 10 % and 60 % (Fig. 3.2b). Within the S peak the immobilisation of Fe through the formation of Fe sulphides (FeS_x) was highest. Below the S peak, the percentage of Fe bound to sulphides on total Fe decreased which was not only due to lower content of mono- and disulphidic bound S but also due to an increase of total Fe.

In Lower Havel, elevated concentrations of mono- and disulphidic-bound S (AVS, CRS) were present at 10-20 cm depth (Fig. 3.2c). The increase in AVS and CRS explained the elevated content of total S below 10 cm depth. S^0 and S_{org} did not change in the upper 20 cm. The immobilisation of Fe through the formation of FeS_x averaged to 12 % of total Fe at 0-10 cm depth. This percentage increased to 40 % at 10-15 cm depth and 63 % at 15-20 cm depth (Fig. 3.2d).

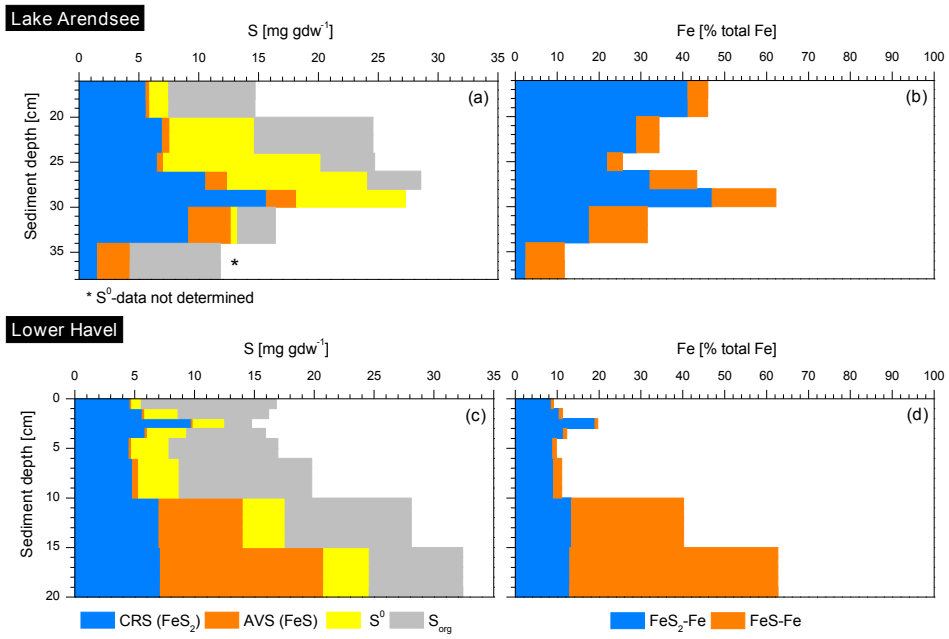

Figure 3.2: Vertical distribution of inorganic sulphur (S) species in sediments of Lake Arendsee (October 2014) and Lower Havel (May 2012). **(a,c)** CRS: chromium reducible S, AVS: acid volatile S, S^0: elemental S and organic S (S_{org}) in mg gdw^{-1}. **(b,d)** Relative contribution of mono- and disulphidic bound Fe to the total Fe content (calculated). Note that the S peak was 10 cm further down-core here, than evident from Fig. 3.1b. Data from Lower Havel are reprinted from Grüneberg *et al.* (2015) under a CC BY license, with permission from Springer, original copyright 2015.

3.4.3 Qualitative and quantitative vivianite analysis

In both waters, i.e. Lake Arendsee and Lower Havel, dark-blue nodules were found in the high-density samples ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$), but not in the low-density samples ($\rho \leq 2.3\,\mathrm{g\,cm^{-3}}$) using a reflected-light microscope. These nodules were identified as the Fe(II)-phosphate mineral vivianite (Figs. 3.3, 3.4). Powder X-ray diffraction pattern showed characteristic reflexes of vivianite whereas in high-density samples without any dark blue nodules vivianite reflexes were missing. The diffraction pattern further confirmed the presence of pyrite, quartz, calcite, mica and plagioclase (Figs. 3.3c, 3.4c).

In Lake Arendsee, vivianite nodules were detected at 26 cm and further

down-core up to 48 cm depth. Highest numbers of vivianite nodules were present between 30 cm and 36 cm depth (Fig. 3.3a). In these layers vivianite had such a high content that it was possible to detect the mineral in bulk sediment using X-ray diffraction (Fig. 3.3c). The transition between vivianite bearing and non-vivianite bearing sediment layers was sharp and already at 26 cm depth numerous small-sized ($< 40\,\mu$m) vivianite nodules were present. The nodules turned out to be spheroidal or irregular in shape and consisted of randomly oriented platy-shaped crystals (Fig. 3.3b). Usually vivianite nodules were smaller than 40 μm in diameter, only between 30 cm and 36 cm depth larger frustules of irregular shape (up to 150 μm in diameter) were present.

High-density samples containing vivianite were characterised by a lower Ca content but had a higher Fe (on average 3.7 times higher), Mn (on average 15 times higher) and P (on average 48 times higher) content compared to samples without vivianite (Table 3.1). The S content was similar for all samples, except for 24-26 cm and 36-38 cm depth, where S content was 7- and 10-times higher, respectively. According to the mass of each high-density sample the amount of P present in these samples accounted for 13.1 $\pm$ 0.4 % of TP in bulk sediment in layers without vivianite and 45.7 $\pm$ 19.9 % of TP in bulk sediment in layers where vivianite was present. The amount of Fe detected in high-density samples accounted for 25 % and 40 % of total Fe in samples with and without vivianite, respectively.

In Lower Havel, vivianite nodules were present in the uppermost sediment layer down to 18 cm depth. Highest numbers of vivianite nodules were present between 2 cm and 10 cm depth, but the number was considerably lower than in sediments of Lake Arendsee (Fig. 3.4a). Between 10 cm and 18 cm depth only some single vivianite crystal aggregates were detected in the high-density samples, and further down-core vivianite was not present. Vivianite nodules with a large size were much more abundant than small nodules ($< 40\,\mu$m) but the overall number of nodules was lower than in samples from Lake Arendsee. Vivianite crystal aggregates had a uniform spherical shape with diameters between 40 μm and 100 μm and consisted of randomly oriented platy-shaped crystals (Fig. 3.4b).

High-density samples containing numerous vivianite nodules (0-10 cm depth)

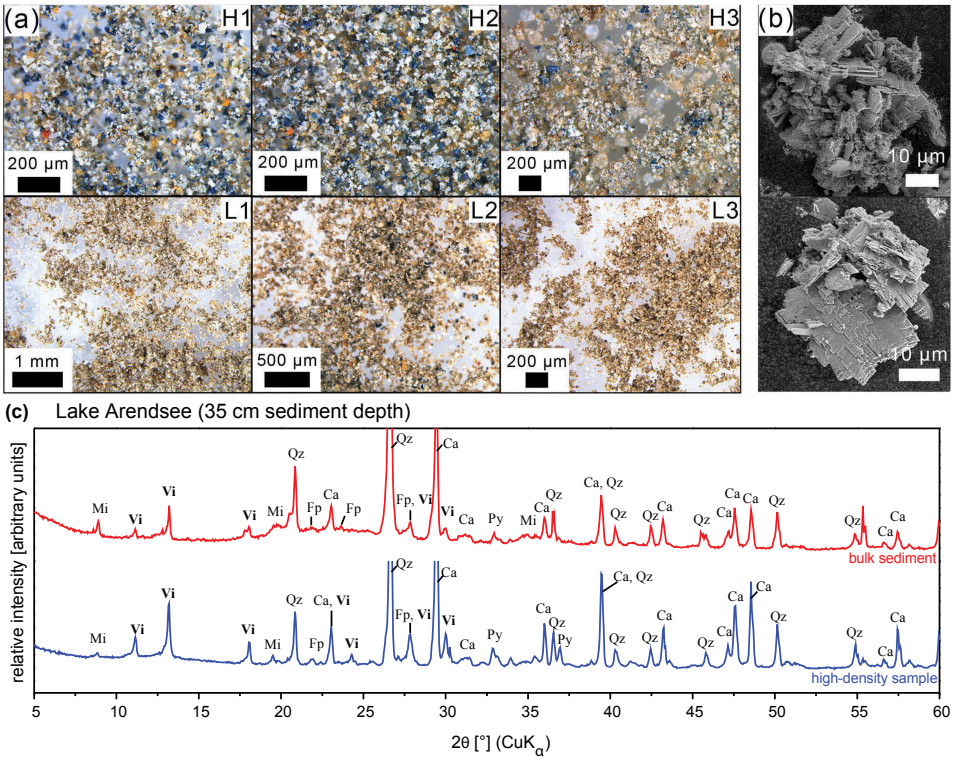

Figure 3.3: Analysis of high-density sediment samples of Lake Arendsee. **(a)** Reflected-light microscope images of high-density ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$, H1-H3) and low density ($\rho < 2.3\,\mathrm{g\,cm^{-3}}$, L1-L3) samples from different sediment depths (positive downward sampling depth) of Lake Arendsee (H1, L1: 27 cm; H2, L2: 35 cm; H3, L3: 41 cm). **(b)** Scanning electron micrographs of dark blue vivianite nodules enriched in high-density samples. **(c)** XRD patterns of bulk sediment (data in red) and high-density samples (data in blue) from 35 cm sediment depth of Lake Arendsee. The pattern confirm the presence of vivianite (Vi). Other minerals identified were calcite (Ca), quartz (Qz), pyrite (Py), mica (Mi) and plagioclase (Fp). For clarity main peaks of calcite and quartz are not shown in total.

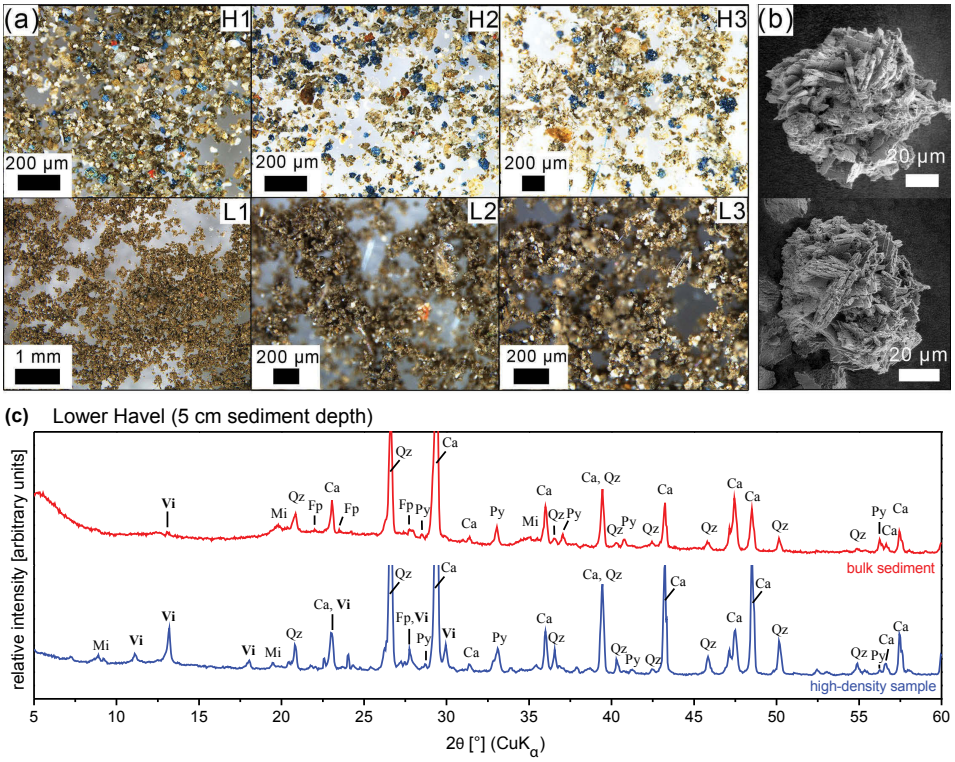

Figure 3.4: Analysis of high-density sediment samples of Lower Havel. **(a)** Reflected-light microscope images of high-density ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$, H1-H3) and low density ($\rho < 2.3\,\mathrm{g\,cm^{-3}}$, L1-L3) samples from different sediment depths (positive downward sampling depth) of Lower Havel (H1, L1: 0.5 cm; H2, L2: 5 cm; H3, L3: 9 cm). **(b)** Scanning electron micrographs of dark blue vivianite nodules enriched in high-density samples. **(c)** XRD patterns of bulk sediment (data in red) and high-density samples (data in blue) from 5 cm sediment depth of Lower Havel. The pattern confirm the presence of vivianite (Vi). Other minerals identified were calcite (Ca), quartz (Qz), pyrite (Py), mica (Mi) and plagioclase (Fp). For clarity main peaks of calcite and quartz are not shown in total.

Table 3.1: Elemental composition and vivianite occurrence of high-density samples ($\rho > 2.3\,\mathrm{g\,cm^{-3}}$) from different sediment depths of Lake Arendsee (February 2014) and Lower Havel (October 2013). The P content of high-density samples (P) is also given as percentage of total P of bulk sediment (P_{Sed}).

Sediment depth [cm]	**vivianite occurrence**	**Ca**	**Fe**	**Mn** [mg gdw^{-1}]	**P**	**S**	**P** [% P_{Sed}]
***Lake Arendsee:* vivianite present at 26-48 cm depth**							
4–6	-	325	1.9	0.3	0.3	2.8	13
8–10	-	339	1.7	0.3	0.1	1.9	13
24–26	-	296	25.9	0.5	0.3	24.9	13
no vivianite present (mean ± SD)		320 ± 22	9.8 ± 13.9	0.4 ± 0.1	0.2 ± 0.1	9.9 ± 13.0	13.1 ± 0.4
26–28	+++	102	44.0	8.3	11.5	2.1	86
28–30	+++	126	35.0	4.2	10.8	3.2	36
32–34	+++	77	33.6	4.6	9.5	2.5	30
34–36	+++	58	42.7	9.1	12.9	1.3	50
36–38	+++	266	33.8	2.5	5.9	16.3	28
38–40	+++	105	35.6	7.6	9.1	2.2	52
40–42	++	111	35.8	9.0	7.9	2.4	39
vivianite present (mean ± SD)		121 ± 68	37.2 ± 4.3	6.4 ± 2.6	9.7 ± 2.3	4.3 ± 5.3	45.7 ± 19.9
***Lower Havel:* vivianite present at 0-18 cm depth**							
0–1	++	245	22.1	1.3	3.1	8.0	7.9
1–2	++	273	22.8	1.5	3.6	8.0	9.8
2–4	++	250	21.8	1.6	3.9	7.1	9.2
4–6	++	264	23.9	2.2	5.5	6.7	12.5
8–10	++	276	23.0	1.7	3.8	8.4	14.3
layers with main vivianite presence (mean ± SD)		262 ± 14	22.7 ± 0.8	1.7 ± 0.4	4.0 ± 0.1	7.7 ± 0.7	10.7 ± 2.6
12–14	+	271	18.6	0.7	1.0	11.2	6.7
16–18	+	283	19.9	0.7	1.5	15.8	9.6
18–20	-	296	22.3	0.6	0.7	32.7	7.3
20–22	-	278	22.3	0.5	0.6	26.4	4.9
no (or hardly any) vivianite present (mean ± SD)		282 ± 11	20.8 ± 1.8	0.63 ± 0.10	0.95 ± 0.40	21.5 ± 9.8	7.1 ± 1.9

number of vivianite nodules: +++ high, ++ medium, + low, - none

had a higher Mn and P content (on average 3- and 6-times higher) than samples without vivianite, whereas Ca and Fe content was similar for all samples (Table 3.1). Sediment layers with vivianite nodules had a two times lower S content than samples from further down core, where only a few or no vivianite crystal aggregates were present. The P concentration of high-density samples containing vivianite accounted for 10.7 ± 2.6 % of sedimentary TP. For high-density samples without vivianite, the amount of P present accounted for 7.1 ± 1.9 % of TP. The Fe content of high-density samples did not show differences between vivianite bearing and non-vivianite bearing samples and accounted for 45.3 ± 3.2 % of total Fe.

3.4.4 Phosphorus fractionation of vivianite

Two different sequential P fractionation schemes (Psenner *et al.*, 1984; Ruttenberg, 1992) were carried out, in order to study the extraction characteristics of vivianite. Following Psenner *et al.* (1984), the synthetic mineral is extracted by two sequential steps: 14 % of vivianite-P was extracted as redox sensitive Fe-bound P (BD-TP) and 84 % as metal-bound P (NaOH-SRP) (Table 3.2). The remaining P forms accounted for less than 2.5 % of TP. A similar result was obtained (28 % BD-TP, 66 % NaOH-SRP) when extracting a high-density sample that was naturally rich in vivianite nodules. Only a minor amount of P was extracted as loosely adsorbed P (NH_4Cl-TP). Following the P fractionation of Ruttenberg (1992) only about 16 % of TP was extracted during CDB extraction which is supposed to represent iron(oxyhydr)oxide-bound P and vivianite-P (Jilbert & Slomp, 2013) (Table 3.2).

Table 3.2: Proportion of sedimentary phosphorus (P) forms according to (Psenner *et al.*, 1984) on total P of synthetic vivianite powder (P_{viv}, surface oxidised, blue appearance) and of a high-density sample ($\rho > 2.3\,g\,cm^{-3}$) naturally rich in sedimentary vivianite. The first two steps of the P speciation according to (Ruttenberg, 1992) are given in brackets.

NH_4Cl-TP (Ex-P)	BD-TP (CDB-P)	NaOH-SRP	NaOH-NRP	HCl-TP	Res-P	Recovery rate
			[% P_{viv}]			
synthetic vivianite						
0.8	13.8	83.9	1.5	0	0	93
(0.2)	(15.8)					
high-density sample naturally rich in sedimentary vivianite						
4.0	28.2	66.3	1.0	0.5	0	102

P speciation according to Psenner *et al.* (1984): NH_4Cl-TP: loosely adsorbed P; BD-TP: redox sensitive P, mainly bound to Fe-(hydr)oxides; NaOH-SRP: metal-bound P, mainly associated with Fe- and Al-oxides; NaOH-NRP: organic-bound P, HCl-TP: P bound in calcium carbonates and apatite; and Res-P: residual P determined after digestion of remaining sediment.

P speciation according to Ruttenberg (1992): Ex-P: loosely sorbed P; CDB-P: iron(oxyhydr)oxide-bound P, vivianite.

3.5 Discussion

3.5.1 Heavy-liquid separation advances the identification and quantification of sedimentary vivianite

Sedimentary vivianite can be directly identified by application of a heavy-liquid separation, as first described by (Rothe *et al.*, 2014). The enrichment of vivianite nodules in high-density samples enables vivianite identification by X-ray diffraction (Figs. 3.3, 3.4), and allows to evaluate the relative contribution of vivianite to sedimentary TP (Rothe *et al.*, 2014). For both Lake Arendsee and Lower Havel, high-density samples with high P content had the lowest molar Fe:P ratios. They were as low as 1.8 (Lake Arendsee) and 2.5 (Lower Havel) which is close to the Fe:P ratio of pure vivianite (Fe:P = 1.5) indicating a high percentage of Fe-P phases in these samples. In contrast, high-density samples without any vivianite nodules, low P and high S content had molar Fe:P ratios larger than 18 indicating elevated contents of sulphidic-bound Fe which is not being able to bind P (Table 3.1).

Considering the mass of each high-density sample relative to the mass of the sample prior to heavy-liquid separation, the corresponding P content gives an upper limit of the amount of vivianite present in the sample. However, P compounds other than vivianite, i.e. P associated with calcium carbonates

and P sorbed onto the surface of iron(oxyhydr)oxides, likely contribute to the P present in the high-density samples.

In contrast, sequential P extraction of vivianite (surface oxidised synthetic vivianite powder and naturally-born vivianite (Table 3.2)) demonstrates that chemical P fractionation methods are not suitable to distinguish between iron(oxyhydr)oxide-bound P and Fe(II)-phosphate minerals, even though they are a widely used tool for the characterisation of P binding forms in soils and sediments (Ruban *et al.*, 1999). Our analysis was performed using a highly crystalline vivianite (as inferred by line width in the XRD pattern), which did not liberate P during a single extraction step, contrary to observations with freshly precipitated vivianite (Williams *et al.*, 1980; Nembrini *et al.*, 1983). Our results suggest that results from the SEDEX extraction scheme typically used for quantifying Fe-bound P (citrate-dithionite-bicarbonate extraction, CDB-P) may vary depending on the proportion of crystalline vivianite in natural sediments. Differences in crystallinity may explain why naturally-born vivianite is liberated to a higher extent than the synthetic vivianite analysed here in the redox sensitive Fe-bound P fraction (Table 3.2). Since Fe(II)-P minerals are stable under reducing sedimentary conditions, an entire liberation of these minerals after addition of a reductant is unlikely. However, both citrate and bicarbonate act as a chelating agent for Fe which can explain a variable liberation of P depending on the crystallinity of the mineral. Our results demonstrate that if freshly-precipitated, less-crystalline vivianite constitutes the predominant fraction in the sediment during sampling then the pool of potentially mobile P (BD-P, CDB-P) may be overestimated.

3.5.2 Occurrence of vivianite is influenced by lake-specific environmental conditions

Most striking in our results, in Lake Arendsee, vivianite was present in deeper sediment horizons (Fig. 3.3) and not in the uppermost layers with a sharp transition between vivianite and non-vivianite bearing layers (Table 3.1). In contrast, in Lower Havel vivianite was present in the upper sediment layers and not in deeper horizons (Fig. 3.4) with a gradual transition between non-

vivianite and vivianite bearing layers (Table 3.1). What are the reasons for the observed pattern in both waters?

In Lake Arendsee the presence of vivianite below 26 cm depth corresponds to a time prior to high anthropogenic nutrient loadings, and the abrupt shift in Fe and P content at the transition from vivianite bearing to non-vivianite bearing layers dates back to the end of the 1930's (Fig. 3.1c). At this time the demand on the lake and its catchment changed and the input of nutrients increased. Due to a long hydraulic residence time of 50-60 yr (Meinikmann *et al.*, 2015) and rising nutrient levels, primary production and hence OM supply toward the sediment increased. This led to an increased demand for oxidants (i.e., O_2, Fe^{3+}, SO_4^{2-}), deteriorating redox conditions and enhanced S^{2-} production through decomposition of OM, specifically putrefaction of organic S (desulphuration) and dissimilatory sulphate reduction (desulphurication). Subsequently, more sedimentary Fe was immobilised by the reaction with S^{2-} and the P binding capacity of the sediment was weakened.

Based upon algal microfossil facies Findlay *et al.* (1998) Lake Arendsee has been eutrophic since the 1940's, but oligo-mesotrophic before that time. Vivianite was present in layers dated back to the beginning of the 20th century. This is in accordance with results from Findlay *et al.* (1998) who reported high P and Fe content and elevated P accumulation rates at a similar time. This observation raises the question where the high amounts of P were originating from in such a low-productive system at this time. What could be the reason for the massive decline in Fe content? Since Lake Arendsee is a karst lake, the intrusion of water rich in P and Fe (Findlay *et al.*, 1998) might explain the high amounts of P and Fe in the sediment and the occurrence of vivianite. The decline in Fe content could also be related to the disconnection of a peatland due to melioration measures close to Lake Arendsee in the 1960's.

In Lower Havel, vivianite nodules were detected in the uppermost centimetre of the sediment, indicating that vivianite formation is an ongoing process, here. However, in deeper sediment layers (below 18 cm depth) vivianite was not present. Compared to Lake Arendsee, in Lower Havel the transition between sediment layers containing numerous vivianite nodules and non-vivianite bearing sediment layers was more gradual which was also

represented in the change of the TP content with depth (Fig. 3.1a, d). In this transition zone, only a very limited number of vivianite crystal aggregates were detected.

The decrease in vivianite abundance and the absence of vivianite at greater depths may be due to dissolution of the mineral through enhanced sediment sulphidization. However, vivianite dissolution is unlikely, here. This is because in Lower Havel oxygen penetration is limited to the uppermost millimetres of the sediment and the zone of SO_4^{2-} reduction is located just below the oxic-anoxic boundary. A pore water study from an organic-rich sediment similar to that of Lower Havel (Rothe *et al.*, 2014) showed that SO_4^{2-} is readily depleted within in the upper 5-7 cm of the sediment. However, in Lower Havel vivianite abundance was highest in the upper 10 cm which matches with the zone where SO_4^{2-} reduction is supposed to be highest. Notably, any vivianite crystal aggregates, neither from the upper 10 cm nor from further down-core, showed signs of pitting from a potential dissolution. Thus, the occurrence of vivianite and the increased P binding capacity of the sediment in the upper 18 cm rather indicate a change of the geochemical conditions in Lower Havel during the last 20 yr but it not reflects the dissolution of vivianite at greater depths (see explanation below).

The observed changes in P binding and the occurrence of vivianite correspond to a time between 1994 and 2006 and were accompanied by a decline in S content (Fig. 3.1). The decline in S burial can be mainly attributed to a decline in OM production observed in Lower Havel during the last 25 yr (Grüneberg *et al.*, 2015). A decrease in productivity leads to both a decline in S sedimentation by settling seston and lower sulphate reduction rates and explains the increased P binding capacity of the sediment and the occurrence of vivianite. The direct effect of changes in water column SO_4^{2-} concentration on S burial is low because SO_4^{2-} is not limiting for phytoplankton and sulphate reducing bacteria (Hordijk *et al.*, 1989; Losher, 1989; Howarth *et al.*, 1992). Moreover, the relative retention of S on the overall water column SO_4^{2-} imported (Likens, 1989) is low in such a shallow system with a water residence time of only 19 d. For example, in Lake Tegel, which is throughflown by River Havel only 3 % of the S import (mainly sulphate) is retained in the sediment

which is due to the short water residence time of 50-90 d (Kleeberg *et al.*, 2012).

In both waters, vivianite bearing sediment layers were characterised by elevated TP content in comparison to non-vivianite bearing sediments (Table 3.1, Fig. 3.5). The TP co-varied with the observed number of vivianite nodules in different sediment depths: for Lake Arendsee, the sharp transisition between vivianite bearing and non-vivianite bearing sediment layers between 24 cm and 26 cm depth was reflected by a steep increase in TP down-core. The increase in TP in vivianite bearing sediment layers (according to P fractionation) was due to increased content of two P forms: redox sensitive Fe-bound P (BD-TP) and metal-bound P (NaOH-SRP) (Fig. 3.1a, d). From the P fractionation of vivianite (Table 3.2) these two P forms are expected to be elevated if vivianite is present in sediments. Moreover, the content of NaOH-SRP in vivianite bearing sediment layers of Lake Arendsee was much higher than in those of Lower Havel (Fig. 3.1a, d). This finding was in accordance with the high number of vivianite nodules detected in high-density samples compared to the number of nodules detected in Lower Havel (Figs. 3.3a, 3.4a). Given the fact that vivianite diffraction peaks could be identified even in a bulk sediment sample (Fig. 3.3c), the contribution of vivianite to overall P burial was certainly higher than in Lower Havel. Based upon the P content of high-density samples, in Lake Arendsee, vivianite-P equated to 46 $\pm$ 20 % of TP below 26 cm depth compared to 11 $\pm$ 3 % of TP at 0-10 cm depth in Lower Havel (Table 3.1). Our estimates of vivianite-P do not intend to give a precise determination, however, they allow to evaluate the relative contribution of vivianite to overall P burial in the studied systems. It is important to note, that vivianite cannot explain the increase in sedimentary TP alone. Due to a relative decrease of immobilised, sulphidic-bound Fe in vivianite bearing sediment layers, iron(oxyhydr)oxides which resisted reductive dissolution in the anoxic sediment (De Vitre *et al.*, 1988; Hyacinthe & Van Cappellen, 2004), contribute to the increase in sedimentary TP, too.

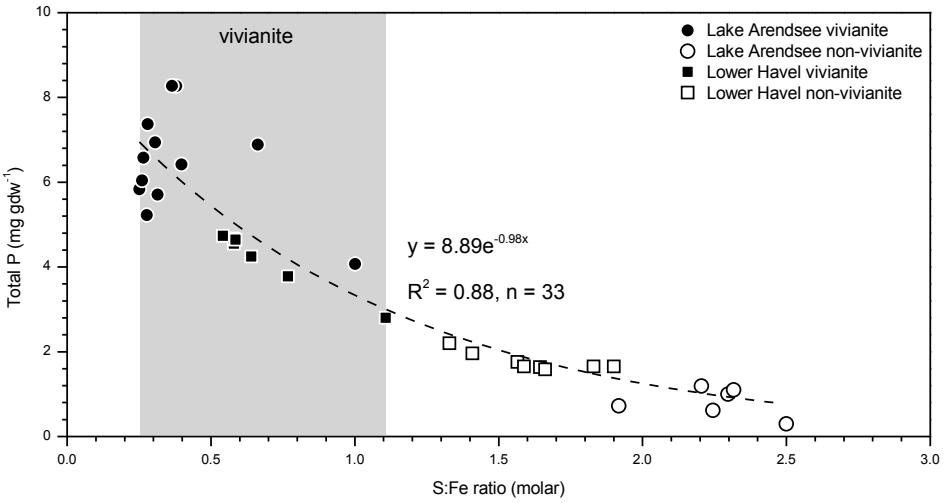

Figure 3.5: Sedimentary total P content of Lake Arendsee and Lower Havel according to the corresponding molar ratio of total sulphur to reactive iron (S:Fe) of the sediment. Vivianite occurs only at a lower S:Fe ratio.

3.5.3 The extend of sulphide formation controls the formation or absence of vivianite

Vivianite was identified in sediment layers which were characterised by a low molar ratio of total S to reactive Fe (S:Fe $\leq$ 1.1; henceforth denoted as "S:Fe") and significantly contributed to an elevated P retention (Fig. 3.5). Given our observational data, the S:Fe ratio is a viable indicator for the conditions that are important drivers behind the formation or absence of vivianite. Notably, the indicator allows to check for a potential presence of vivianite before performing any elaborate analysis.

The formation of vivianite crucially depends on the availability of the two major ions it consists of: Fe^{2+} and PO_4^{3-}. The prevailing redox conditions thereby govern the fate of both ions in the sediment. Under oxic conditions, Fe is not reduced and the PO_4^{3-} released during the decomposition of OM is efficiently sorbed. Under anoxic conditions, ferric Fe and sulphate are used as alternative electron acceptors by heterotrophic bacteria leading to elevated production of Fe^{2+}, PO_4^{3-} and S^{2-} favouring the formation of secondary mineral phases such as vivianite and Fe sulphides (FeS_x). Vivianite and FeS_x

formation occur simultaneously (see Figs. 3.3c, 3.4c) as long as the supply of Fe^{2+} exceeds the production of S^{2-}. The molar S:Fe ratio is an indicator of the availability of S relative to that of Fe. The higher the S:Fe ratio, the higher the contribution of sulphidic-bound Fe to total Fe. Assuming that the formation of Fe monosulphide is the primary formation product between ferric Fe compounds and H_2S,

$$2\,FeO(OH) + 3\,H_2S \longrightarrow FeS + S^0 + 4H_2O, \text{(Søndergaard } \textit{et al.}\text{, 2002)}$$

a molar S:Fe ratio smaller than 1.5 indicates that there is more reactive Fe available than it could be bound by S^{2-}. Thus, not all reactive Fe is captured in sulphidic form and vivianite formation is favoured. In both waters, the S:Fe ratio was below that threshold and a decrease of sulphidic-bound Fe was observed in layers where vivianite was present (Figs. 3.1, 3.2). The occurrence of reduced Fe phosphates also has been shown for anoxic, organic-rich marine sediments and vivianite has been proposed to be a likely P form (März *et al.*, 2008; Jilbert & Slomp, 2013). In these systems, vivianite is expected to occur below the sulphate-methane transition. This is where redox conditions are low enough to favour the production of Fe^{2+} but S^{2-} already precipitated allowing vivianite to form (Hsu *et al.*, 2014). Also these systems should be characterised by a molar S:Fe ratio smaller than 1.5 indicating an excess of Fe relative to the production of S^{2-} and vivianite formation should not be restricted by the supply of Fe.

Due to eutrophication, i.e. a primarily enhanced P supply, the P-binding capacity of a sediment will be exceeded leading to a higher P mobility and less or no vivianite formation. A higher productivity leads to a higher OM supply toward the sediment which has consequences for the formation of vivianite. First, there is a higher demand for oxidants leading to a deterioration of redox conditions and higher reduction rates of ferric Fe and SO_4^{2-} (Holmer & Storkholm, 2001). Second, there is more S^{2-} produced because OM is specifically enriched in S compared to Fe (Redfield ratio: $C_{106}N_{16}P_1S_{0.7}Fe_{0.05}$, (Stumm & Morgan, 1981)). Sulphides are formed by both desulphuration and dissimilatory sulphate reduction leading to a higher degree of sediment sulphidization.

The former can be quite significant in overall sedimentary hydrogen sulphide production, e.g. 5.1 - 53 % (Dunnette *et al.*, 1985). Moreover, eutrophication is often accompanied by considerable inputs of SO_4^{2-} leading to its higher availability and high rates of its consumption (Holmer & Storkholm, 2001; Zak *et al.*, 2006). Third, the OM itself can react with Fe forming a metal organic complex (Lalonde *et al.*, 2012). The higher the sedimentary S:Fe ratio, the less reactive Fe seems to be available reducing the potential of vivianite to form (Fig. 3.5) because more Fe is bound in sulphidic form. Thus, under eutrophic conditions there is a negative feedback evolving through the enhanced supply of OM lowering the sedimentary P retention capacity due to less vivianite.

Aquatic systems naturally high in reactive Fe may compensate better for a eutrophication induced decrease in P retention than systems low in Fe. This implies, that an artificial supply of Fe to systems with a high level in OM, P and SO_4^{2-} can be used as a successful measure of lake restoration leading to increased P retention through vivianite formation (Kleeberg *et al.*, 2013; Rothe *et al.*, 2014). To ensure a lasting effect on P burial, Fe has to be supplied in surplus compensating for the losses through FeS_x formation (Kleeberg *et al.*, 2013) and the reaction with OM (Lalonde *et al.*, 2012). At which magnitude vivianite finally forms in different types of sediments depends on multiple factors and remains to be further investigated. The formation of the mineral is also controlled by the availability of OM rich in P, the concomittant liberation of Fe^{2+} and PO_4^{3-} into the pore voids of the sediment, the activity of microorganisms and resorption of PO_4^{3-} onto the surface of remaining iron(oxyhydr)oxides.

3.6 Conclusions

Vivianite was identified in surface sediments of two organic-rich freshwater sediments. The application of a heavy-liquid separation of sediment, leading to an enrichment of vivianite nodules in the high-density sediment fraction, appears to provide a reliable method to identify the mineral within the sediment matrix. The proof of vivianite in two contrasting freshwater systems and

in different sediment depths, i.e. formed exclusively in the past or at present, revealed that the formation of vivianite strongly depends on the prevailing environmental conditions and is indicated by the molar ratio of total S to reactive Fe (S:Fe). Vivianite can be formed and contributes to a significantly higher P retention, as long as not all the available Fe in the sediment is converted to Fe sulphides. These conditions are met in sediments characterised by a S:Fe ratio smaller than 1.5. As a result of eutrophication, an increased supply of OM toward the sediment surface can lead to a temporarily increased retention of P and S. A longer lasting increase in OM supply of sediments favours the release of sulphides, and the formation of insoluble Fe sulphides leading to a lack of available Fe and to less or no vivianite formation. This weakening in sedimentary P retention, representing a negative feedback mechanism in terms of water quality, could be partly compensated by harmless Fe amendments.

Chapter 4

The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments

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4.1 Abstract

This article reviews the nature, occurrence and environmental relevance of the authigenic ferrous iron phosphate mineral vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) in waterlogged soils and aquatic sediments. We critically discuss existing work from freshwater and marine systems, laboratory studies and microbial batch culture experiments aiming to deduce common characteristics of the mineral's occurrence, and the processes governing its formation. Vivianite regularly occurs in close association with organic remains in iron-rich sediments. Simultaneously, it is a biogenic mineral product of metal reducing bacteria. These findings suggest that vivianite nucleation in natural systems is directed by the activity of such bacteria and crystal growth is particularly favoured within protected microzones. Taking into account recent findings from coastal marine sediments where vivianite authigenesis has been shown to be coupled to the anaerobic oxidation of methane, small-scale microbially mediated reactions appear to be crucial for the formation of vivianite. Small-scale heterogeneity within the sediment matrix may also explain why saturation calculations based upon bulk pore water constitutions often fail to accurately predict the occurrence of the mineral. Vivianite is not restricted to a specific trophic state of a system. The mineral forms in oligotrophic- as well as in eutrophic waters. However, depending on the iron inventory, the extent of organic matter production determines the relative contribution of iron sulphide formation to the iron pool, and the concentration of inorganic phosphate and Fe^{2+} in pore waters. Thus, vivianite authigenesis is also governed by bulk chemical conditions such as the rate of sulphide formation relative to that of Fe^{2+} production. This situation allows stimulation of vivianite formation by iron supplementation aimed at restoring eutrophic lakes. Promising results from coastal marine sediments suggest that vivianite authigenesis is of significance for P burial in the marine realm. Determining the impact of vivianite authigenesis on a global scale has so far largely been ignored, despite its likely importance.

4.2 Introduction

Vivianite is the most common stable iron phosphate mineral forming in sedimentary environments (Nriagu, 1972; Emerson, 1976; Berner, 1981a). This mineral occurs worldwide in various aquatic systems, such as freshwater and marine sediments, and in terrestrial systems such as waterlogged soils, bogs, hydrothermal deposits and archaeological settings as well as in wastewater sludges (Table 4.1).

Despite of the widespread occurrence of vivianite, most notably in lacustrine sediments, its origin, mode of formation, and significance in the global phosphorus (P) cycle are not well understood. Of particular interest are the recent observations from anoxic marine sediments which suggest that the authigenic formation of reduced iron (Fe) phosphates is of much greater importance for the burial of P than previously assumed (Slomp *et al.*, 2013; Dijkstra *et al.*, 2014; Egger *et al.*, 2015).

The retention of P in aquatic sediments consists of a cascade of three main processes (Boers *et al.*, 1998): "deposition on the sediment, transformation of mainly organic P and immobilization, and burial or percolation to deeper sediment layers." The immobilization of P and the ability of a sediment to retain P is influenced by the characteristics of the depositional environment, such as the nature of the input source material and the sedimentation rate including the prevailing redox conditions (Ruttenberg & Berner, 1993). The fixation of P within sediments thereby depends on the transport of orthophosphate between solid particles, adsoption-desorption mechanisms, chemosorption, biological assimilation and mineral nucleation including the formation of iron and calcium phosphates such as viviante and apatite (Søndergaard *et al.*, 2001).

Bound P may be organic-bound P or inorganic-bound P. Organic-bound P originates from organic matter, which is "often the principle carrier of P to the sediments" and "quantitatively one of the most important reservoirs of P in marine sediments" (Ruttenberg & Berner, 1993). In a succession of mineralization processes, organic-bound P can be liberated and the orthophosphate released may be bound in microbial biomass, sorbed by ferric (oxyhydr)oxides,

aluminium hydroxides, clays and silicates or bound in secondary phosphate minerals authigenically formed during early sediment diagenesis. Authigenic phosphate minerals can constitute a significant pool among the long-term P inventory of sediments.

Most prominently, carbonate fluorapatite is a major burial sink in the ocean (Ruttenberg & Berner, 1993; Slomp *et al.*, 1996; Schulz & Schulz, 2005). In addition to calcium phosphates, ferrous phosphates may significantly contribute to P retention in anoxic sediments, particulary if the sediments are anoxic but non-sulfidic (Gächter & Müller, 2003). Moreover, also oxidised Fe compounds such as ferric (oxyhydr)oxides and ferric phosphates can persist in reductive environments, significantly contributing to P binding under these conditions (Hyacinthe & Van Cappellen, 2004; Lehtoranta *et al.*, 2009). The fundamental processes of sediment diagenesis, authigenic iron mineral formation, and reactivity of iron-bearing minerals, however, are only briefly addressed in this review, since those were recently reviewed by Roberts (2015).

By the pioneer work of Einsele (1936) and Mortimer (1941) the tight coupling between the Fe and the P cycle in aquatic environments has been revealed. It is well known that ferric (oxyhydr)oxides form at oxic/anoxic boundaries in lakes and marine water bodies (Ruttenberg & Berner, 1993), crucially influencing the behaviour of orthophosphate, arsenate and trace metals as a result of their scavenging capacity (see Gunnars *et al.*, 2002, and references therein). In the absence of oxygen, the degradation of organic matter by dissimilatory Fe and sulphate reducing bacteria as well as methanogens leads to the liberation of ferric Fe compounds, the production of sulphides (S^{2-}) and the formation of iron sulphides (FeS_x), thus, counteracting the functioning of ferric (oxyhydr)oxides in trapping P (Roden & Edmonds, 1997). Simultaneously, ferric (oxyhydr)oxide-P compounds may undergo reductive dissolution in the presence of S^{2-} (Sugawara *et al.*, 1957; Smolders & Roelofs, 1993; Murray, 1995). However, the increased liberation of solutes, such as orthophosphate, Fe^{2+} and Mn^{2+}, in response to organic matter decomposition also leads to favourable conditions for the formation of other, non-sulfidic, authigenic minerals such as carbonates (siderite, carbonate fluorapatite) and phosphates (vivianite) (Suess, 1979).

This review will summarize existing knowledge on sedimentary vivianite, including its characteristics and appearance, methodological identification, and its occurrence in various sedimentary settings. From this literature synthesis, we discuss the methodological limitations of vivianite identification and present the factors that appear to controlling the mineral. We also include a conceptualised model of the most important processes governing vivianite formation in sediments, arising from the literature on microbial batch culture experiments. This review will also discuss the quantitative importance of vivianite authigenesis for P burial, its ecological role in aquatic systems, and the importance of vivianite in the restoration of eutrophied lakes. The review concludes with a short perspective on further challenges to be faced in order to uncover the role of vivianite in the global P cycle.

4.3 Vivianite characteristics and appearance

Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, named after the English mineralogist John Henry Vivian (1785-1855), is a hydrous phosphate of ferrous Fe, and crystallizes in the monoclinic system. Vivianite is the Fe-rich end-member of the vivianite mineral group ($M_3(XO_4)_2 \cdot 8\,H_2O$, where M= divalent Mg, Mn, Fe, Co, Ni, Cu, Zn, and X=P or As). The mineral's structure consists of single ($FeO_2(H_2O)_4$) and double ($Fe_2O_6(H_2O)_4$) octahedral groups, linked to each other by PO_4 groups and $H_2O{-}H_2O$ hydroxyl bonds (Rouzies & Millet, 1993). The magnetic properties of vivianite are well known: the mineral is paramagnetic but undergoes antiferromagnetic transition at a Néel temperature of 12 K (Meijer *et al.*, 1967; Frederichs *et al.*, 2003).

Vivianite is colourless and translucent in its pristine state. Upon exposure to air, vivianite is known for its vivid bluish to green appearance, which is due to a gradual oxidation of Fe(II) (Hush, 1967) (Fig. 4.1). Manning *et al.* (1991) identified pale blue crystals of vivianite in sediments of mesotrophic Narrow Lake, Alberta and noted that the weak colour indicated a low concentration of ferric ions in the vivianite.

The oxidation characteristics of vivianite have been studied in detail: when ferrous Fe is oxidised, water molecules are substituted by hydroxyl groups

Table 4.1: Compilation of the natural occurrence of vivianite (v) in aquatic and terrestrial systems worldwide, drawn from the scientific literature between 1970 and 2015.

System	Location	Identification	Remarks	Reference
Sediment of Freshwater Lakes	Lake Åsrum, Norway	by eye	v not present in the underlying lagunal and marine sediments	Rosenqvist (1970)
	Great Lakes, USA	by eye, microscopy	v not directly associated with organic remains although these materials were abundant	Nriagu & Dell (1974)
	Lake Ur, Germany	by eye	meromictic bog lake	Tessenow (1974)
	Lago Maggiore, Italy	by eye, SEM, XRD, Mössbauer spectroscopy	v depth layer not in accordance with saturation calculations	Nembrini *et al.* (1983)
	Toolik Lake, Alaska	by eye, SEM-EDX	ultra-oligotrophic arctic lake, v does not occur at the sediment surface but only below the oxic-anoxic interface	Cornwell (1987)
	Narrow Lake, Canada	by eye, XRD	v only present in the deep southern basin where the molar S:Fe ratio was higher than in the shallow northern basin	Manning *et al.* (1991)
	Lake Biwa, Japan	by eye, XRD, X-ray fluorescence	manganoan v, high sulphide concentration cause vivianite dissolution	Nakano (1992); Murphy *et al.* (2001)
	Lake Bussjösjön, Sweden	by eye	present in preindustrial non-sulfidic sediments	Olsson *et al.* (1997)
	Baptiste Lake, Canada	XRD, Mössbauer spectroscopy	influence of groundwater rich in Fe^{2+} and phosphate	Manning *et al.* (1999)
	Lake Baikal, Russia	by eye, SEM-EDX, XRD, IR spectroscopy	manganoan vivianite, v grains contain inclusions of plagioclase and pyrite, formation in microenvironments	Fagel *et al.* (2005); Sapota *et al.* (2006); Minyuk *et al.* (2013)
	Laguna Potrok Aike, Argentinia	by eye, SEM-EDX, XRD	indirect signs of microbially mediated v formation, uranium-thorium dating of v	Nuttin *et al.* (2013); Vuillemin *et al.* (2013)
	Lake Pavin, France	XRD	v detected on sinking particles, role of polyphosphates in precipitation of reduced Fe phosphates	Cosmidis *et al.* (2014)
	Lake Groß-Glienicke, Germany	by eye, SEM-EDX, XRD	v formation triggered by Fe supplement	Rothe *et al.* (2014)
	Lake Ørn, Denmark	SEM-EDX, XRD	identification by XRD on bulk sediment	O'Connell *et al.* (2015)
Sediment of Rivers	Potomac River, USA	by eye, SEM-EDX	major control on the occurrence of v is the presence or absence of amorphous ferric oxi-hydroxides	Hearn *et al.* (1983)
	Mississippi River, USA	by eye, X-Radiography	v consists of radial aggregates of 1-3 mm in diameter and occurs together with other diagenetic minerals (siderite, pyrite, calcite, dolomite, hematite)	Bailey *et al.* (1998)
	Havel River, Germany	by eye, SEM, XRD	occurrence of v associated with a decreased sulfidization in response to a lower primary productivity	Rothe *et al.* (2015)
	Old Birmingham Mainline Canal, UK	SEM-EDX	v coexisted with biogenic structures and pyrite framboids	Dodd *et al.* (2003)

Sediment of Canals	Salford Quays, UK	SEM-EDX, XRD, Raman spectroscopy, XANES, EXAFS	highly contaminated, organic-rich canal bed sediments	Taylor & Boult (2007); Taylor *et al.* (2008)
Waterlogged Soils	Organic soil, Denmark	XRD, Mössbauer spectroscopy	v neoformation in response to Fe(III) reduction following anoxic soil incubation	Heiberg *et al.* (2012)
	Meadow soil, Denmark	by eye, SEM-EDX, XRD, Mössbauer spectroscopy	dissolution precipitation experiments, v shows slow precipitation kinetics	Walpersdorf *et al.* (2013)
	Paddy field soil, Japan	by eye, SEM-EDX, XRD	v attached to aged rice roots	Nanzyo *et al.* (2010, 2013)
Bogs	Swamps, Auckland Area, New Zealand	by eye, XRD	XRD detection sucessfull after the minerals exposure to air	Rodgers (1977)
	River bog, Denmark	XRD	v coexisted with siderite, calcite and occasionally pyrite	Postma (1981)
Marine Sediments	Amazon Fan, Brazil	by eye, SEM-EDX	v occurs below the depth of total sulphate depletion	Burns (1997)
	Yung-An Ridge, South China Sea	SEM-EDX, XRD, Raman spectroscopy, IR spectroscopy	magnesium-rich vivianite, v formation influenced by methane induced sulfidization	Hsu *et al.* (2014)
	Bothnian Sea, Baltic Sea	SEM-EDX, XRD, μXRF, XANES	anaerobic oxidation of methane triggers v formation	Egger *et al.* (2015)
Other	Wastewater sludge	SEM-EDX, XRD, Mössbauer spectroscopy	P removal through Fe reduction-induced P precipitation	Frossard *et al.* (1997); Zhang (2012)
	Hydrothermal deposits	by eye	v retains its deep colour even where intensively altered	Robertson (1982); Rodgers *et al.* (1993)
	Archaelogical settings	by eye	v present on the surface of bones and other human remains, important function of microorganisms proposed	Tessadri (2000), McGowan & Prangnell (2006, and references therein)

EXAFS: extended X-ray absorption fine structure
IR spectroscopy: infrared spectroscopy
μXRF: micro X-ray fluorescence
SEM-EDX: scanning elecetron microscopy with energy dispersive X-ray spectroscopy
XANES: X-ray absorption near edge structure
XRD: powder X-ray diffraction

to offset the valence change. Vivianite oxidation proceeds slowly at room temperature and stabilises at a Fe^{3+} concentration of 50 % total Fe (Rouzies & Millet, 1993). Nriagu (1972) noted that blue oxidised vivianite was almost indefinitely stable under laboratory conditions. Rouzies & Millet (1993) pointed out that at values higher than 50 % Fe^{3+}, vivianite alters to metavivianite ($Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot 6\,H_2O$). Further oxidation is favoured at higher temperatures, and results in the formation of poorly crystalline mixed valence or ferric Fe phosphate phases, for example lipscombite ($Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$), santabarbaraite ($Fe_3^{3+}(PO_4)_2(OH)_3 \cdot 5\,H_2O$) and strengite ($FePO_4 \cdot 2\,H_2O$) (Nriagu, 1972; Nriagu & Dell, 1974; Pratesi *et al.*, 2003). In a calcareous medium, vivianite oxidation results in the formation of a poorly crystalline Fe oxide (lepidocrocite, $\gamma{-}Fe^{3+}O(OH)$) (Roldán *et al.*, 2002). The oxidation of vivianite may explain why additions of vivianite prevent Fe deficiencies in plants growing on calcareous soils (Rombolà *et al.*, 2003).

Vivianite regularly contains significant amounts of Mn and/or Mg, which substitute for Fe in the vivianite lattice. In general, the amount of trace metals in vivianite is an indicator of the surrounding geochemical conditions, and vivianite formed in polymetallic ore deposits contains higher abundances of trace elements than minerals formed in reducing aquatic environments (Tessadri, 2000). Regularly, crystal aggregates appear to consist of "manganoan" vivianite (Nakano, 1992), or of a mixture of vivianite and ludlamite ($(Fe, Mn, Mg)_3(PO_4)_2 \cdot 4\,H_2O$) or baricite ($(Mg, Fe)_3(PO_4)_2 \cdot 8\,H_2O$). Nodules enriched in Mn have been reported mostly from freshwater systems such as lake- and canal sediments (Nriagu & Dell, 1974; Tessenow, 1974; Nakano, 1992; Fagel *et al.*, 2005; Sapota *et al.*, 2006; Taylor *et al.*, 2008). Baricite, the Mg analogue of vivianite, was reported from an Fe-rich cold seep sediment off western Taiwan (Hsu *et al.*, 2014), and the authors noted that this Mg-rich vivianite might not be as common in freshwater systems as in marine systems because of low magnesium concentration in lacustrine and riverine sediments. Burns (1997) detected vivianite nodules "with considerable amounts of Mg" in Amazon Fan sediments, Brazil.

Moreover, Frossard *et al.* (1997) found sand-sized vivianite and baricite in air-dried waste-water sludge. Vivianite forms an important component of

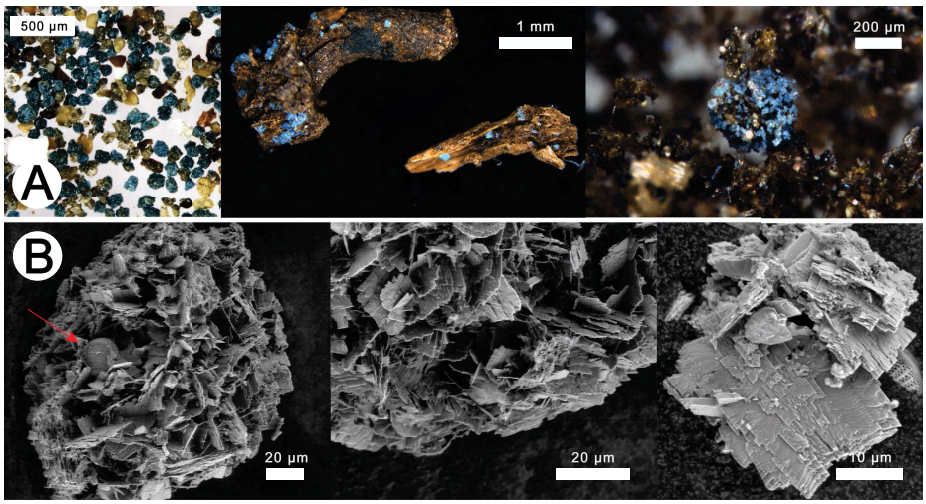

Figure 4.1: Microscopic appearance of vivianite nodules separated from lacustrine sediments. A) (from left to right) Reflected-light microscope images of vivianite nodules from surface sediments of Lake Groß-Glienicke, Germany; from a reflooded wetland now forming a shallow lake (Polder Stangenhagen, Germany); and from Lake Stechlin, Germany. B) Scanning electron micrographs of vivianite nodules separated from lacustrine sediments. Spherical vivianite nodules separated from sediments of Lake Groß-Glienicke, Germany (images to the left and middle), showing inclusions of a diatom shell (arrow mark) and other organic debris. A vivianite concretion separated from Lake Arendsee, Germany (image to the right) consists of small, flat, broad crystals. Reflected-light microscope image of vivianite from Lake Groß-Glienicke (image to the left), and electron micrographs are taken from Rothe *et al.* (2014) (images to the left and middle) and Rothe *et al.* (2015) (image to the right) under a Creative Commons Attribution license.

metal cycling in contaminated sediments as confirmed in a study from Taylor *et al.* (2008) that showed that early diagenetic vivianite may act as a sink for Zn and other contaminants such as As during its formation. In another study, Liu & Zhao (2007) emphasized the high effectiveness of synthesized vivianite nanoparticles for the in situ immobilization of heavy metals, such as copper, in soils.

Vivianite nodules and concretions are often of similar habitus. They are described as "hemispheres" (Müller & Förstner, 1973), "spherical aggregates" (Hearn *et al.*, 1983), "tightly packed spherules" (Henderson *et al.*, 1984) and "large oolithic" nodules (Nakano, 1992) with diameters ranging from a few micrometres to centimetres. The aggregates consist of "radiating lath-shaped crystals and needle-like masses" (Taylor *et al.*, 2008),"distinct elongated prismatic" (Zwaan & van der Sluys, 1971) or "rod shaped" (Frossard *et al.*, 1997) crystals. In a laboratory experiment Zelibor *et al.* (1988) studied the morphological characteristics of vivianite crystals grown in agar gels. The authors suggested that the combination of the gel medium in the pore spaces and the natural electric field in the upper sediments, could be contributing causes to explain the spherical aggregates of vivianite crystals found in nature. In a study about the occurrences of vivianite in Quaternary swamp and surface deposits in the Auckland area, New Zealand, Rodgers (1977) noted that the "spheroids" consisted of "millimetre long needles" which "often appear to radiate from a void".

The rough surface and the "euhedral form of crystals on particle surfaces" (Hearn *et al.*, 1983), as well as inclusions of diatom shells and other organic debris (Rothe *et al.*, 2014), are a natural indicator of the authigenic origin of vivianite (Fig. 4.1). From the random orientation of the crystallities on the surface of vivianite microconcretions, Sapota *et al.* (2006) concluded that pore spaces in the sediment were not confined by extensive compaction, and hence vivianite formation must have been taken place in an early diagenetic environment in surface sediments. Other investigators (Cosmidis *et al.*, 2014; Rothe *et al.*, 2014, 2015) identified vivianite nodules within the first centimetre of freshwater lake and river sediments. These findings allow for the conclusion that vivianite can form rapidly during early diagenetic transformations. In

contrast, in an attempt to date authigenic vivianite from Laguna Potrok Aike, Argentinia using uranium-series, Nuttin *et al.* (2013) concluded that the formation of vivianite "seems to be a long lasting process after burial and does not permit estimating precise and reliable diagenetic precipitation ages".

4.4 Methods of vivianite identification

By far the most simple approach includes the identification of vivianite nodules by naked eye taking advantage of the characteristic colour change of the mineral on exposure to air (Rosenqvist, 1970; Olsson *et al.*, 1997; Brauer *et al.*, 1999; Nanzyo *et al.*, 2013; Rothe *et al.*, 2014), and subsequent microscopic and/or chemical analysis. Sedimentary vivianite has been identified and characterised by methods including X-ray powder diffraction (XRD) (Postma, 1981; Manning *et al.*, 1991; Taylor *et al.*, 2008; Heiberg *et al.*, 2012; Cosmidis *et al.*, 2014; Rothe *et al.*, 2014), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (Hearn *et al.*, 1983; Stamatakis & Koukouzas, 2001; Dodd *et al.*, 2003), infrared (IR) spectroscopy (Fagel *et al.*, 2005; Hsu *et al.*, 2014), Raman spectroscopy (Taylor *et al.*, 2008; Milucka *et al.*, 2012) and Mössbauer spectroscopy (Nembrini *et al.*, 1983; Manning *et al.*, 1991; Frossard *et al.*, 1997). Additionally, the magnetic properties of vivianite have been used to identify and quantify vivianite in sediments (Frederichs *et al.*, 2003; Rothe *et al.*, 2014).

Because vivianite is highly sensitive to oxidation, its identification by XRD has been reported to be difficult by some authors (Bricker III & Troup, 1973; Olsson *et al.*, 1997; März *et al.*, 2008), suggesting that vivianite rapidly looses its characteristic crystal structure upon exposure to air. However, this assertion has been questioned by others (Rodgers, 1977; Suess, 1979; Manning *et al.*, 1991; Frossard *et al.*, 1997; Rothe *et al.*, 2014). That the crystal structure of vivianite remains stable upon exposure to air at room temperature is supported by the oxidation characteristics of vivianite (Rouzies & Millet, 1993), and the observation that the gradually oxidised mineral is stable under laboratory conditions (Nriagu, 1972).

Successful XRD detection appears to depend on the amount of vivianite

present in the sample, the size and crystallinity of nodules, and the density of reflexes from other mineral phases which may interfere with those of vivianite (Emerson & Widmer, 1978). The XRD measurements of bulk sediment samples, and samples naturally enriched in vivianite, showed that about a 5 % weight of vivianite was necessary to detect the mineral by XRD, i.e. that at least the three most intensive peaks are clearly visible (Rothe *et al.*, 2014).

The direct and unambiguous identification of vivianite in sediments is not always easy because phosphate minerals usually comprise only a small part of a sediment matrix (Lindsay *et al.*, 1989). Thus, indirect approaches such as pore water equilibrium calculations, and sequential P extractions have been widely used to predict the occurrence of vivianite in natural systems. However, simultaneously these indirect approaches limit the validity and specificity of findings with regard to the factors and conditions leading to the formation of the mineral.

Density separation of water-free sediment using different concentrations of a sodium polytungstate solution ($3\,Na_2WO_4 \cdot 9WO_3 \cdot H_2O$) is an easy and reliable approach to enrich sedimentary vivianite in the high-density ($\rho > 2.3\,g\,cm^{-3}$) sediment fraction (Rothe *et al.*, 2014, 2015). The enrichment of natural vivianite allows a direct identification of vivianite by XRD, a detailed microscopic analysis of mineral grains, and a quantitative determination of the amount of vivianite present in the sediment. An alternative approach to determining the amount of vivianite in the high-density sediment fraction, is magnetic hysteresis measurements, which take advantage of the paramagnetic nature of viviante (Rothe *et al.*, 2014).

4.4.1 Thermodynamic calculations: potentials and limitations

Ultimately, crystal growth depends on thermodynamic principles and a mineral nucleates from solution if the mineral saturation state is above the equilibrium value. The solubility constant of vivianite has been examined by Rosenqvist (1970) and Nriagu (1972), and the principle stability of vivianite and the conditions favourable for its formation have been derived from these thermodynamic considerations (Nriagu, 1972; Nriagu & Dell, 1974; Postma,

1981). Vivianite is stable at pH conditions from 6 to 9, and its formation is favoured by high activities of ferrous Fe and orthophosphate in pore waters. Such conditions are commonly found in organic and Fe-rich waterlogged soils and sediments where reducing conditions persist but sulphide (S^{2-}) production is low.

Thermodynamic equilibrium calculations have been widely used to predict the occurrence of vivianite and other authigenic minerals in various environmental settings. However, supersaturated pore water may only serve as an indicator for the conditions at which the formation of a specific mineral is possible. Supersaturation does not directly indicate an active mineral formation because reaction kinetics ultimately control the crystallisation of mineral grains. In their study, Emerson & Widmer (1978) demonstrated by flux calculations that vivianite growth is rather controlled by surface processes, than by the diffusion of solutes. Subsequently, other investigators confirmed that there is no equilibrium control by vivianite with respect to pore water orthophosphate and Fe^{2+} concentration (Postma, 1981; Boers & de Bles, 1991; Walpersdorf *et al.*, 2013), and that supersaturated pore waters may or may not indicate the occurrence of the mineral within a sediment (Rothe *et al.*, 2014) (Fig. 4.2).

Some authors have noted the weakness of pore water evidence of vivianite determined from ion activity product calculations. Cornwell (1987) noted in his study about authigenic P minerals in an artic lake that “pore water evidence is not sufficient to determine authigenic mineral precipitation: the mineral must be identified within the sediment”. Murphy *et al.* (2001) concluded that discrepancies between pore water observations (supersaturation) and proven mineral precipitation indicates that “vivianite formation and stability in sediments is not completely understood” (referencing Boers & de Bles (1991)). In their review about phosphate chemistry in lake sediments Syers *et al.* (1973) concluded: “Application of the solubility product is useful for predicting which P compounds are thermodynamically stable or which P compounds can theoretically form. It is difficult, if not impossible, however, to take the findings obtained with ”pure“ systems in the laboratory and solubility predictions based on thermodynamics and to extrapolate these

to the extremely complex environment in lake sediments, in which reactions kinetics may be modified by other dissolved species and solid phases."

Solubility product calculations should be done with care because the validity of results is limited due to the following constraints: (i) calculations are based upon activity coefficients which are not very accurate, especially for trivalent ions; (ii) there is complexation, in particular in the presence of organic compounds which increases the solubility and kinetically retards nucleation; and (iii) small particles (nano-/micrometresized) normally have higher solubilities than do large bulk particles. Furthermore, it is important to consider that all solubility product calculations are based upon macroscopic measurements for example using pore water samplers with a theoretical resolution of milimetres to centimetres (Hesslein, 1976). However, mineral nucleation and crystal growth take place on a nano- to micrometre scale, and might be associated with specific solid phases and the activity of microorganisms. Thus, small-scale in situ conditions within microenvironments are not well represented by such saturation calculations (Dodd *et al.*, 2003; Glasauer *et al.*, 2003).

4.4.2 Sequential phosphorus extraction procedures

To determine the chemical character of P binding forms in soils and sediments, sequential P fractionation techniques use solvents with different chemical properties including acids, bases and reducing agents (Ruban *et al.*, 1999; Lukkari *et al.*, 2007). There are various protocols available, with different operationally defined P forms. Most of them address inorganic P forms (Ruban *et al.*, 1999) to differentiate between loosely adsorbed (exchangeable) P, Fe-bound P, apatite-P, and residual P.

Ferric Fe compounds and the P associated with these compounds (by adsorption or by chemical binding) are sensitive to redox changes and may be liberated under anoxic conditions. Thus, the Fe associated P from strictly anoxic sediments has been attributed to stable ferrous Fe phosphate minerals such as vivianite, or to ferric Fe phases which resist reductive dissolution (Hyacinthe & Van Cappellen, 2004). However, none of the existing extraction

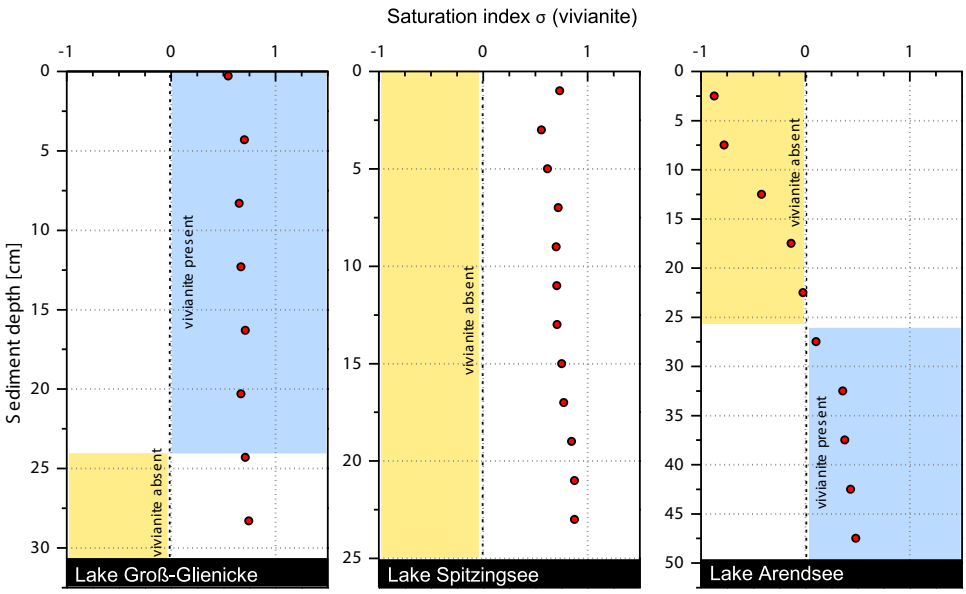

Figure 4.2: Pore water saturation indices of vivianite compared to the actual occurrence of vivianite at different sediment depths from three different lakes. Saturation index $\sigma < 0$ indicates undersaturation, $\sigma > 0$ indicates supersaturation, and $\sigma = 0$ indicates equilibrium with respect to vivianite. Speciation calculations were performed using the computer code PhreeqC (Parkhurst & Appelo, 1999). Saturation indices were calculated according to the following equation (Habraken *et al.*, 2013): $\sigma = ln\left[\left(\frac{\mathrm{IP}}{\mathrm{K}_{sp}}\right)^{(1/\nu)}\right]$. Here IP is the ionic activity product, expressed using the species stoichiometry, ν is the number of growth units in the material, taking into account growth by ions in a classical nucleation way (in case of vivianite $\nu = 13$), and $\mathrm{K_{sp}}$ is the solubility activity product of vivianite ($\mathrm{K}_{sp} = 1 \cdot 10^{-36}$, (Nriagu, 1972)). Lake Groß-Glienicke is a mesotrophic, shallow lake [mean depth 8 m] in NE Germany; Lake Spitzingsee is a small oligotrophic, alpine lake in S Germany; and Lake Arendsee is a eutrophic, deep karst lake in N Germany. Pore water profiles were taken on October 2013 (Lake Groß-Glienicke), November 2012 (Lake Spitzingsee) and May 2012 (Lake Arendsee). Data from Lake Groß-Glienicke are taken from Rothe *et al.* (2014).

schemes differentiates between ferrous and ferric Fe-P compounds, nor specifically targets vivianite. Thus, the occurrence of reduced Fe phosphates may be plausible in these cases, however, a direct identification of the specific Fe phosphate mineral is missing.

Based upon results presented by Williams *et al.* (1980) and Nembrini *et al.* (1983), freshly precipitated vivianite has been considered to be liberated within the redox-sensitive Fe-bound P fraction (Jilbert & Slomp, 2013; Dijkstra *et al.*, 2014) of the SEDEX sequential P extraction (citrate-dithionite-bicarbonate extraction, CDB-P, (Ruttenberg, 1992)). In contrast, Rothe *et al.* (2015) noted that synthetic and natural vivianite was not entirely liberated in one single extraction step (bicarbonate-dithionite, BD-TP) targeting the Fe-bound P phases of the sequential extraction procedure of Psenner *et al.* (1984). The results Rothe *et al.* (2015) presented suggest that vivianite liberation depends on the crystallinity of the mineral and highly-crystalline vivianite is not entirely liberated during the extraction targeting Fe-bound P (for example CDB extraction of the SEDEX procedure (Ruttenberg, 1992), BD extraction of the procedure of Psenner *et al.* (1984)).

It appears that the extraction characteristics of vivianite are not totally clear and this further complicates the interpretation of sequential P extractions with regard to the occurrence of reduced Fe phosphates and vivianite. Although P extractions estimate of the portion of P that may become bioavailable under certain environmental conditions and the portion of P which is stably bound, the many types of naturally occurring P species classified within a few extraction steps, mean that sequential P extraction procedures are only an approximate approach (Lukkari *et al.*, 2007; Hupfer *et al.*, 2009).

4.5 Vivianite occurrence and formation mechanisms

Vivianite has been reported from reductive environments and occurs in sediments of lakes, rivers, canals, peat bogs, swamps, river fans and cold seep settings; it has been also identified in waterlogged soils (Table 4.1). Records include quaternary, postglacial, modern and surface deposits. Vivianite also occurs in sewage sludge and as a weathering product in hydrothermal and

pegmatic deposits and as a secondary mineral in Fe-bearing ore veins. Vivianite formation is not limited to soils and sediments, the mineral has been also identified within the water column of a meromictic Fe-rich crater lake (Cosmidis *et al.*, 2014). The mineral appears to be more common in freshwater than in marine systems.

The conditions at which vivianite is found in situ correspond well with the theoretically derived stability of vivianite in aquous media: the mineral is stable in reducing environments, and if pore waters have sufficiently high orthophosphate and Fe^{2+} concentration, and S^{2-} is not present in high amounts (Nriagu, 1972). Indeed, authigenic vivianite has been consistently reported to occur in reducing sediments that are organic- and Fe-rich but where S^{2-} production is low, meaning free sulphides readily precipitate to form insoluble metal sulphides and no H_2S is present (e.g. Rosenqvist, 1970; Nriagu & Dell, 1974; Henderson *et al.*, 1984; Cornwell, 1987; Nakano, 1992; Brauer *et al.*, 1999; Bradbury & Dean, 1993; Manning *et al.*, 1999; Rothe *et al.*, 2014).

Direct association of vivianite crystal aggregates with organic remains appears to be a common feature, although it is not ubiquitous. Tessenow (1974) detected spherical vivianite nodules in a bog lake (Lake Ursee, Germany) and some of these nodules were grown on the remains of leaves and fibres. Stoops (1983) found vivianite associated with decaying roots, or alone inside root channels in a soft bog of the Belgian Campine. Henderson *et al.* (1984) reported vivianite encrusting fragments of decayed wood and fossil bone in swamp, lake and surface deposits of the Auckland area (New Zealand), and recently, Nanzyo *et al.* (2013) demonstrated that vivianite crystal aggregates grow on and within decaying rice roots in a paddy field soil, Japan. Also Stamatakis & Koukouzas (2001) reported that vivianite frequently replaces leaves and faecal pellets in lacustrine clayey diatomite deposits, Thessaly, Central Greece. Moreover, vivianite has been identified in teeth and bones of dead bodies buried in waterlogged conditions, in close proximity to a source of Fe (McGowan & Prangnell, 2006). Other investigators have found vivianite crystallities in close association with algal remains such as diatom shells.

Vivianite formation appears to be favoured under organic-rich conditions which typify the minerals occurrence and its environment (Henderson *et al.*,

1984). Readily degradable organic debris may enhance the development of reducing microenvironments, and simultaneously serve as an important orthophosphate source. Such conditions are common in the vicinity of effluent from water sewage plants (Hearn *et al.*, 1983), septic plume systems (Robertson *et al.*, 1998), and in sediments receiving high anthropogenic wastewater and nutrient loadings (Goslar *et al.*, 1999; Dodd *et al.*, 2003; Taylor *et al.*, 2008). Moreover, P supply may be naturally enhanced by P-rich ground water percolating through sediments (Manning *et al.*, 1999). Vivianite has been identified in all these settings.

It is well accepted that Fe oxyhydroxides play an important role in vivianite formation. As these compounds efficiently scavenge orthophosphate, but are subject to microbial and chemical reduction (Melton *et al.*, 2014), they serve as a source for Fe^{2+} and orthophosphate, and may therefore act as an important precursor phase for vivianite. Tessenow (1974) concluded that the "reduction of sedimented Fe(III)hydroxophosphate complexes" and the "rapid solution of Fe and [...] orthophosphate" under anoxic conditions is of particular importance for the accumulation of Fe^{2+} and orthophosphate in pore waters, and finally vivianite precipitation. Fagel *et al.* (2005) proposed for Lake Baikal, in Siberia, Russia, that the ferrosoferric hydroxyphosphates ($Fe^{2+}_{n_1}Fe^{3+}_{n_2}(PO_4)_{n_3}(OH)_{2n_1+3n_2}(H_2O)_{n_4}$) accumulating at the sediment surface dissolve further below, in more reducing conditions, and subsequently lead to direct precipitation of vivianite from pore waters (citing Nriagu & Dell, 1974). A similar conclusion was drawn by Sapota *et al.* (2006), suggesting that Fe oxyhydroxide-rich particles may have adsorbed sufficient amounts of orthophosphate during periods of slow sedimentation and subsequently allowed vivianite to form. Manning *et al.* (1991) showed that in Narrow Lake, Alberta, Canada, the main sink of orthophosphate switches, with increasing depth of burial, from adsorption on ferric oxides to incorporation into vivianite. Hearn *et al.* (1983) identified that the presence or absence of amorphous ferric oxy-hydroxides controlled the occurrence of vivianite in Potomac River sediments (USA). However, they found vivianite concentrated in a coarse-sand dredge spoil in a surface layer which contained less ferric oxy-hydroxides than did the layers without vivianite. They proposed that these amorphous Fe

phases react with pore water orthophosphate to form stable ferric phosphates preferentially to the formation of vivianite.

The reductive dissolution of Fe oxyhydroxides and the accompanying release of orthophosphate appear to be important triggers for vivianite formation. In meromictic Lake Pavin (Massiv Central, France), Cosmidis *et al.* (2014) attributed the precipitation of vivianite to the reductive dissolution of Fe (oxyhydr)oxides and mixed valence Fe phosphates. In laboratory incubation experiments with soil slurries, Heiberg *et al.* (2012) and Walpersdorf *et al.* (2013) showed that vivianite formed during anoxic treatment in response to reductive dissolution of Fe(III). In wastewater sludges, Zhang (2012) detected vivianite after addition of solid Fe(III), and proposed that P removal was triggered through an "Fe reduction-induced precipitation".

The supply of S relative to that of Fe appears to be another important factor influencing the formation of vivianite, by controlling Fe^{2+} concentration in pore waters. Vivianite preferentially forms in "non-sulfidic" systems, where the rate of S^{2-} production does not exceed that of the Fe^{2+} supply (Berner, 1981b; Gächter & Müller, 2003; Rothe *et al.*, 2015). If almost all reactive Fe in the sediment is bound by S^{2-}, pore water Fe^{2+} concentrations are too low to allow vivianite to form. However, FeS_x and vivianite commonly coexist as long as sufficient Fe is available (Stoops, 1983; Olsson *et al.*, 1997; Brauer *et al.*, 1999; Dodd *et al.*, 2003; Vuillemin *et al.*, 2013; Rothe *et al.*, 2015).

It has been proposed that the sedimentary S:Fe ratio can be used to indicate the conditions that explain the presence or absence of vivianite (Rothe *et al.*, 2015). A S:Fe ratio smaller than 1.5 indicates that there is excess Fe relative to that of S, and vivianite formation is not restricted by the supply of Fe (see below). Olsson *et al.* (1997) found vivianite only in pre-1900 sediments which had a low S content. In contrast, vivianite was absent from post-1900 sediments which had a higher S content. The authors proposed, that under low primary production and low S supply, sediments acted as an efficient P sink through the formation of vivianite but increased S^{2-} production significantly decreased the sequestration of Fe-associated P forms (Olsson *et al.*, 1997). Through eutrophication and the elevated production of organic matter as well as through increased SO_4^{2-} levels, the supply of S relative to that of Fe

is favoured, leading to deteriorated conditions for vivianite formation.

In many marine sediments there is excess dissolved S^{2-} relative to dissolved Fe^{2+} (Berner, 1970, 1981a), because the SO_4^{2-} concentration is about 100 times higher in seawater than in freshwater. In marine sediments, biogenic apatite is a much more common authigenic phosphate phase than vivianite (Ruttenberg & Berner, 1993; Burns, 1997). The role played by reduced Fe(II) phosphates in P burial in these systems has largely been disregarded so far. However, vivianite may be favoured in estuarine and fan sediments, as well as in productive shelf seas which are characterised by a higher supply of Fe and organic matter than the deep ocean. Until now, only a few studies have identified vivianite in such systems (Burns, 1997; Hsu *et al.*, 2014; Egger *et al.*, 2015).

Recent studies, however, indicate that the formation of reduced Fe phosphates is favoured in organic-rich sediments both within, and below the sulphate/methane transition zone (SMTZ). This is zone is where high concentration of orthophosphate and ferrous Fe are present in pore waters, and S^{2-} has already precipitated (März *et al.*, 2008; Jilbert & Slomp, 2013; Slomp *et al.*, 2013; Hsu *et al.*, 2014). For the Bothnian Sea, Egger *et al.* (2015) provided evidence for vivianite formation below a shallow SMTZ, suggesting that methane plays a crucial role in providing conditions favourable for vivianite authigenesis. The results indicated that the anaerobic oxidation of methane drives a sink-switching from Fe oxide-bound P to vivianite. Egger *et al.* (2015) concluded that vivianite "likely represents an important burial sink for P in coastal systems worldwide". Thus, the formation of reduced Fe phosphates such as vivianite might be of much greater importance for the global P cycle than previously assumed.

It is well known that vivianite forms as a result of oxidation-reduction reactions in sediments. Vivianite is often accompanied by an assemblage of authigenic minerals which might be precursors for vivianite, such as ferric and mixed valence Fe phases, or that form at the expense of vivianite. In addition to FeS_x, these authigenic minerals include Fe carbonates (such as siderite (Suess, 1979; Brauer *et al.*, 1999)), Fe silicates (such as limonite (Müller & Förstner, 1973)) or other phosphate minerals (such as hydroxylapatite, anapaite

(Stamatakis & Koukouzas, 2001)). However, the formation of these mineral assemblages close to each other cannot be explained by macroenvironmental mineral equilibria alone, which indicates that various microenvironments with different conditions must have existed besides each other during mineral formation (Stoops, 1983). This conclusion is in accordance with the discrepancies reported from pore water equilibrium calculations, and the limitations arising from such calculations. The findings suggest that small-scale processes within the sediment matrix governed by the activity of microorganisms, as well as the porous, heterogenous sediment matrix itself, play an important function in mineral nucleation.

4.6 The role of microorganisms in vivianite formation

Microorganisms influence the formation of vivianite in sediments both directly and indirectly. Direct effects are mediated by the supply of orthophosphate, Fe^{2+} and S^{2-}, due to their active contribution in organic matter mineralization and the use of electron acceptors such as Fe^{3+} and SO_4^{2-}. The indirect effects are by consuming O_2, NO_3^-, Fe^{2+}, and other electron acceptors, thus changing redox conditions, and producing CO_2 which lowers the pH. Thus, pore water saturation conditions are mediated by biological processes, and the formation of secondary minerals may be biogenic (Suess, 1979; Vuillemin *et al.*, 2013). Bacteria can thereby induce mineral precipitation by modifying the microenvironment surrounding their cells (such as concentrating ions and changing pH) and/or acting as nucleation sites to overcome kinetic barriers (Sánchez-Román *et al.*, 2015). Thus, nucleation on a biological template can occur before nucleation in a homogenous solution.

Laboratory batch culture experiments show that microorganisms can direct the precipitation of vivianite and other authigenic minerals such as siderite, apatite, magnetite (Fredrickson *et al.*, 1998; Glasauer *et al.*, 2003), suggesting that microorganisms are also actively involved in the formation of these minerals under natural, sedimentary conditions (Vuillemin *et al.*, 2013). The formation of vivianite has been linked to the activity of dissimilatory metal reducing bacteria (DMRB), coupling organic carbon oxidation to Fe(III) re-

duction (Fredrickson *et al.*, 1998; Zachara *et al.*, 1998; Glasauer *et al.*, 2003; O'Loughlin *et al.*, 2013). The DMRB transformed hydrous ferric oxide (HFO) into siderite and vivianite if Fe^{2+} complexing ligands, such as HCO_3^- and HPO_4^{2-} were present in the culture medium. Zachara *et al.* (1998) observed, that biogenic vivianite and siderite were formed through dissimilatory reduction of synthetic and natural Fe oxides, and that the formation of vivianite preceded that of siderite.

Vivianite had rapid precipitation rates (7-14 d) and the crystallinity was enhanced in the presence of anthraquinone-2, 6-disulfonate (AQDS, a humic acid analogue) (Zachara *et al.*, 1998; Glasauer *et al.*, 2003). In the absence of complexing ligands, biogenic Fe^{2+} sorbed to HFO and promoted its solid-state conversion to magnetite or "green rust" (Fredrickson *et al.*, 1998). Green rust is a layered ferrous-ferric Fe hydroxide and acts as a reactive intermediate which slowly converts (within month) into vivianite in the presence of orthophosphate (Hansen & Poulsen, 1999). Glasauer *et al.* (2003) reported that under conditions of low orthophosphate, and hence P-limited cell growth, Fe^{2+} and orthophosphate concentration were insufficient for vivianite and magnetite formation and goethite was formed instead.

From the spatial separation of microorganisms and vivianite crystal aggregates, Glasauer *et al.* (2003) concluded that the mineral did not nucleate on the cell surface, but that microorganisms directed the precipitation within cell-influenced microenvironments. In contrast, Sánchez-Román *et al.* (2015) provided evidence for vivianite nanoglobules formed on the surface of the bacterial cell wall, and within the matrix of exopolymeric substances, of *Tessaracoccus lapidicaptus*, a nitrate-reducing, and facultatively anaerobic, Actinobacterium isolated from the Rio Tinto basin, Spain. The presence of vivianite crystals on the surface of bacterial cell walls suggests that microorganisms act as nucleation sites for vivianite within sediments, and provide microenvironments where crystal growth is particularly favoured. There are also indications that the particular microorganisms involved in the anaerobic oxidation of methane (AOM) with sulphate and Fe can biomineralise vivianite. Milucka *et al.* (2012) presented evidence for Fe- and phosphate-rich particles appearing within *Desulfosarcina and Desulfococcus* cells in AOM

aggregates, which points to the presence of vivianite in these cells.

Recently, the formation of oceanic phosphorite deposits (including apatite and carbonated fluorapatite) (Omelon *et al.*, 2013) has been recognized as occurring in close association with polyphosphate-accumulating bacteria, which locally enhance inorganic phosphate concentration, and hence phosphorite saturation (Schulz & Schulz, 2005; Goldhammer *et al.*, 2010). The polyphosphate identified in the diatom *Skeletonema* spp. appears to play a critical role in formation of the dispersed calcium phosphate grains found in many marine sediments which act as mineral templates for biogenic apatite (Diaz *et al.*, 2008). For meromictic Lake Pavin, Massiv Central, France, Cosmidis *et al.* (2014) proposed that the activity of polyphosphate accumulating bacteria may trigger Fe-phosphate precipitation. In the water column, and at the bottom, of this Fe-rich but sulphate-low crater lake, the authors detected significant accumulation of vivianite and observed polyphosphate granules within microorganisms of which some of them were associated with Fe.

Vivianite authigenesis in sediments appears to be highly dependent on the sediment microstructure, and the specific geochemical conditions within protected microenvironments. In the case of vivianite, the development of these microenvironments is generally favoured in organic-rich, non-sulphidic, but anoxic, sedimentary settings. Vivianite formation eventually takes place in protected pore voids which are maintained by the activity of microorganisms (Fig. 4.3).

The nucleation of mineral grains may either appear directly from pore water solution, or is directed by microbial cell walls and other particulate organic remains providing a biological template for vivianite crystals. Cosmidis *et al.* (2014) alternatively proposed, that vivianite could also form due to the progressive reduction of Fe(III) in mixed valence Fe-phosphates during sinking through a anoxic water column, or in bottom sediments, similar to the conversion of green rust into vivianite under reducing orthophosphate-rich conditions as reported by Hansen & Poulsen (1999) (Fig. 4.4).

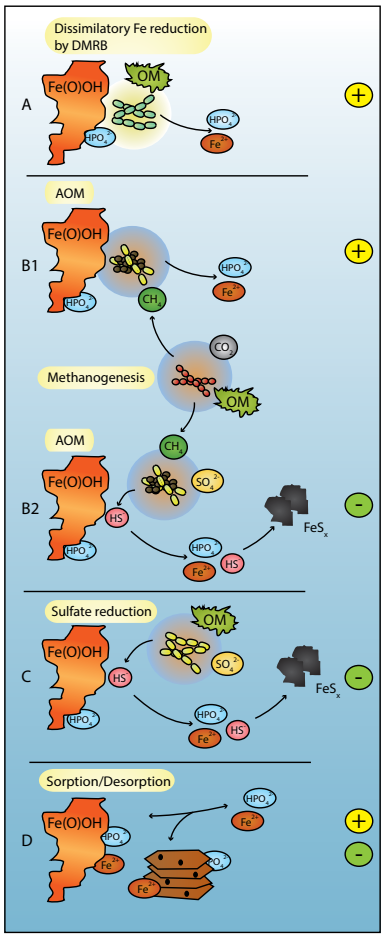

Figure 4.3: Vivianite formation affected by cell-induced microenvironments and sorption/desorption processes. Organic matter (OM) and Fe (oxyhydr)oxides (Fe(O)OH), representing the principle source material for Fe^{2+} and orthophosphate in pore waters, are the most important compounds for vivianite authigenesis. The processes which control the concentration of both ions in pore water are mediated by microbial activity and/or take place on a micro-/nanometre scale. Processes leading to an increase of Fe^{2+} and orthophosphate concentration include: (A) the reduction of iron by dissimilatory metal reducing bacteria (DMRB) and (B1) the anaerobic oxidation of methane (AOM) with iron, thus, promoting vivianite authigenesis. Processes lowering the concentration of Fe^{2+} in pore water by formation of iron sulphides (FeS_x) include: (B2) AOM with sulphate and (C) sulphate reduction, thus, counteracting vivianite authigenesis. (D) Sorption and desorption of Fe^{2+} and orthophosphate on sediment particles decrease or increase the concentration of both ions in pore water, thereby affecting vivianite authigenesis.

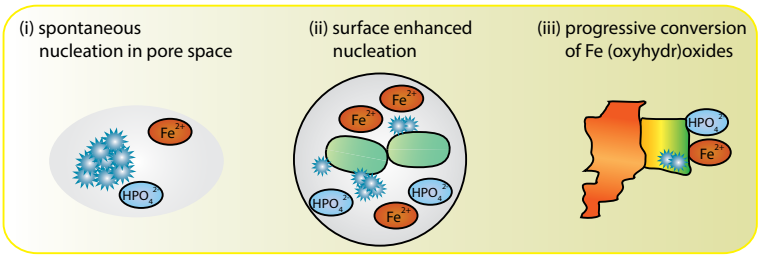

Figure 4.4: Three proposed mechanisms of vivianite formation in aquatic sediments: (i) vivianite may nucleate directly from pore solution, (ii) its nucleation is directed by a biological template such as the cell wall of microorganisms or organic remains, or (iii) it forms through progressive conversion of ferric iron compounds under reductive, Fe^{2+}- and orthophosphate-rich conditions.

4.7 Ecological role of vivianite in aquatic systems

In many lakes, P is the ultimate limiting nutrient that govern primary productivity. Through vivianite formation in surface sediments, P sequestration can be significantly increased. This increase has consequences for the orthophosphate availability for primary producers in the overlying water, which in turn may result in a change of the N:P stoichiometry and altered algal assemblages.

Immediate effects of vivianite formation on a lake's P budget are expected, if: (1) vivianite formation significantly contributes to benthic P retention, (2) the formation of the mineral takes place in the recent, early diagenetic sediment layers which are still in close connection to the overlying water, and (3) vivianite is not readily solubilised, and its post-depositional mobility is low.

The observations made on vivianite's occurrence in sediments and its crystal habit document the early diagenetic nature of vivianite as described in section 2. The cases in which vivianite has been identified directly at the sediment surface, or within the first centimetre of the sediment (for example Cosmidis *et al.*, 2014; Rothe *et al.*, 2014, 2015) can serve as direct proof of its early diagenetic formation. However, vivianite authigenesis does not necessarily occur in close proximity to the sediment surface, but can appear also several centimetres deep within the sediment, as it is common for many marine

settings and in oligotrophic systems with deeper oxygen penetration.

In contrast, vivianite is often detected in sediment several metres to hundreds of metres deep, and has been used as a proxy to reconstruct paleoenvironmental conditions (for example Brauer *et al.*, 1999; Fagel *et al.*, 2005; Sapota *et al.*, 2006; Minyuk *et al.*, 2013; Vuillemin *et al.*, 2013). However, it appears to be difficult to reconstruct the age of the nodules and their mode of formation, (rapid and immediate after sediment deposition, or slow and long lasting) (Nuttin *et al.*, 2013; Vuillemin *et al.*, 2013). Nonetheless, the presence of vivianite in deep sediment layers demonstrates that vivianite can persist many thousands of years within the sediment.

Apart from its common occurrence in lacustrine sediments, not much is known about the quantitative contribution of vivianite in P burial. In recent years, efforts have been made to further elucidate the role of vivianite in P sequestration, using combinations of different kinds of chemical extractions (Egger *et al.*, 2015), or taking advantage of an enrichment of vivianite nodules after sediment preparation (Rothe *et al.*, 2014). According to Rothe *et al.* (2014, 2015) and Egger *et al.* (2015), 20-40 % of total P was bound in vivianite, exemplifying that vivianite authigenesis can be of substantial relevance in P sequestration.

In marine sediments, the role of vivianite in P sequestration has so far largely been ignored. However, as already mentioned in the preceeding sections (section 4, section 5), vivianite authigenesis may be of significance in marine sediments rich in organic matter and Fe. What has been proposed for the Baltic Sea and Black Sea by Jilbert & Slomp (2013) and Dijkstra *et al.* (2014), and recently demonstrated in the Bothnian Sea sediments (Egger *et al.*, 2015) is that authigenic vivianite is a significant burial sink for P in Bothnian Sea sediments. This suggests that the mineral represents an important P sink in coastal sediments worldwide, whereupon its formation is closely coupled to the anaerobic oxidation of methane.

In lacustrine systems, increased P retention through vivianite authigenesis may partly be induced by the occurrence of plant roots, and the activity of tube-dwelling macrozoobenthos such as chironomid larvae. In both cases, the redox zonation of the sediment is altered by introduction of oxygen into

the sediment, leading to zones of Fe (oxyhydr)oxide accumulation and concomittant orthophosphate sorption from the surrounding anoxic pore water (Hölker *et al.*, 2015). Moreover, orthophosphate release and its subsequent accumulation in these zones is favoured through enhanced microbial degradation of organic compounds originating from plant root exudates and the chironomid's metabolism. The development of microzones with favourable conditions for vivianite formation may particularly occur after the plant roots have died, and burrows are abandoned. Indeed, vivianite crystal aggregates have been detected attached to aged rice roots in a paddy field soil (Nanzyo *et al.*, 2013), and the authors discussed the role of an Fe plaque surrounding the roots for vivianite crystal growth. For chironomids, the effects on benthic element cycling and element budgets and particularly the long-term effects on P sequestration remain largely unknown (Hölker *et al.*, 2015). However, given our current knowledge of the occurrence of vivianite and the role of microbes in biogeochemical cycling of elements and the associated biogenic mineral formation, benthic tube-dwellers may positively affect vivianite authigenesis in surface sediments.

Vivianite has been detected in many anthropogenically influenced sedimentary settings, most notably where P availability was increased. These findings allow for the conclusion that vivianite authigenesis might have been favoured by increased nutrient loadings, and the mineral's occurrence mirrors human impact on aquatic nutrient cycling. Egger *et al.* (2015) concluded that coastal eutrophication leads to a vertical upward migration of the sulphate/methane transition zone within the sediment, shifting the zone of favourable conditions for vivianite formation closer to the sediment surface. It was postulated that anthropogenic fertilization of coastal areas throughout the last century therefore increased the role of vivianite authigenesis in many coastal surface sediments (Egger *et al.*, 2015). In contrast, in many lacustrine systems, increased nutrient supply led to accelerated eutrophication, including deteriorated oxygen and redox conditions, and the appearance of S^{2-} in the water column, indicating a loss of Fe associated P binding capacity of the sediments. In some cases, vivianite seems to be present only in pre-industrial sediments representing low nutrient levels, low organic matter production and low S

supply during its deposition (Olsson *et al.*, 1997; Rothe *et al.*, 2015).

The extent of organic matter production and its supply to the sediment have consequences for the formation of vivianite. A higher organic matter supply leads to a higher demand for oxidants, resulting in deteriorated redox conditions and higher reduction rates of Fe^{3+} and SO_4^{2-} (Holmer & Storkholm, 2001). Because organic matter is specifically enriched in S compared to Fe (Redfield ratio: $C_{106}N_{16}P_1S_{0.7}Fe_{0.05}$, (Stumm & Morgan, 1981)), more S^{2-} is produced by desulphuration and dissimilatory sulphate reduction than is produced with a lower organic matter supply, leading to a higher degree of sediment sulphidisation (Berner, 1981a). This affects the availability of Fe^{2+} in pore waters, and hence also vivianite authigenesis. Neither the SO_4^{2-} concentration nor the rate of organic matter supply by itself are absolute predictors for the bacterial sulphate reduction rate. Nevertheless, both processes are crucial for the extent of sulfide- and thus vivianite formation.

Recently, Rothe *et al.* (2015) has proposed that the sedimentary S:Fe ratio (total sulphur to reactive iron; reactive iron represents the proportion of total iron extracted by sediment digestion with aqua regia) can be used as a diagnostic and powerful means to interpret former diagenetic conditions, i.e. the stages by which the sediment was being progressed. The higher the S:Fe ratio, the more Fe is bound in sulfidic form, and the less Fe is available for vivianite formation. In four lacustrine and riverine systems, sediments with vivianite had a higher P content and a lower molar S:Fe than if vivianite was absent (Fig. 4.5).

Generally, a sedimentary molar S:Fe ratio < 1.5 (total sulphur to reactive iron) indicates conditions favouring vivianite formation, because mineral growth is not restricted by the supply of Fe^{2+} (Rothe *et al.*, 2015). A molar S:Fe ratio ≥ 1.5 indicates an excess of S^{2-} relative to the supply of Fe^{2+}, and most of the Fe will be bound in sulfidic form. Evidently, vivianite is not an indicator of nutrient-rich (eutrophic) or nutrient-scarce (oligotrophic) conditions but rather its occurrence mirrors the extent of Fe oxide availability to that of S^{2-} production under a given supply of organic matter. Thus, depending on the Fe inventory, there is a range of nutrient conditions (oligotrophic - eutrophic) under which vivianite formation is favoured. The molar S:Fe ratio

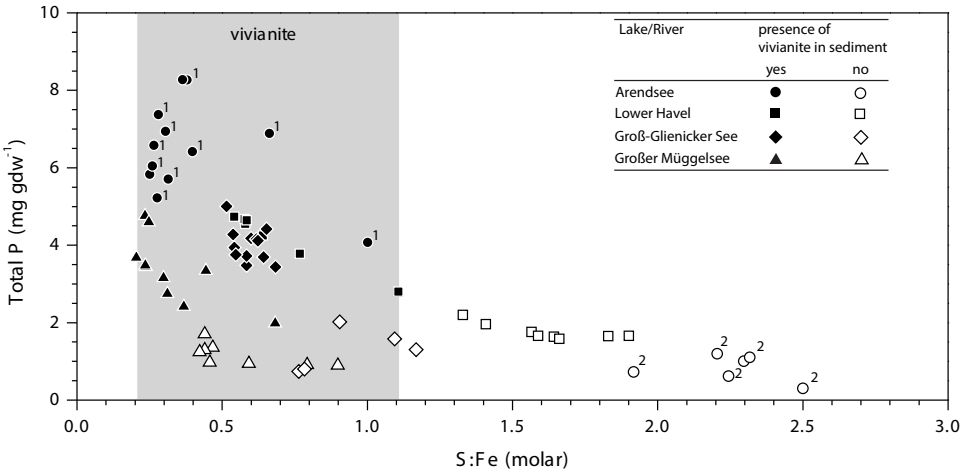

Figure 4.5: The sedimentary molar S:Fe ratio (total sulphur to reactive iron) as an indicator of conditions favourable for vivianite authigenesis. Vivianite occurs only at low S:Fe ratios (< 1.1), and simultaneously contributes to a comparably higher total phosphorus (P) content ($> 2\,\mathrm{mg\,gdw^{-1}}$). Data originate from three lakes and one river in NE Germany (Lake Arendsee, eutrophic; Lake Groß-Glienicke, mesotrophic; lowland river Lower Havel, eutrophic; Lake Großer Müggelsee, eutrophic). For Lake Arendsee, vivianite formed in the past (1) but not at present (2), due to major qualitative changes in the sediment's chemical composition reflected by very high S:Fe ratios in non-vivianite bearing sediment layers. Surface sediments of Lake Großer Müggelsee are characterized by a very high iron content (approximately $90\,\mathrm{mg\,gdw^{-1}}$) resulting from a mining impacted catchment area which explains a comparatively low total phosphorus content at low S:Fe ratios. Figure extended from Rothe *et al.* (2015) under a Creative Commons Attribution license.

can be used as a simple indicator to screen and select sediments for a further analysis of vivianite.

In marine systems, SO_4^{2-} concentrations ($\tilde{2}700\,mg\,L^{-1}$) are high enough that bacterial sulphate reduction rates are independent of SO_4^{2-} in the water. In contrast, in freshwater systems bacterial sulphate reduction rates are affected by the quantity and quality of organic matter, and also by the concentration of SO_4^{2-}. Although often much higher, freshwater dissolved SO_4^{2-} concentrations are still regarded to be typically: $< 27\,mg\,L^{-1}$ (Capone & Kiene, 1988), 9.6-28.8 $mg\,L^{-1}$ (Caraco *et al.*, 1989), 4.8-29.8 $mg\,L^{-1}$ (Marino *et al.*, 1990), 0.96-19.2 $mg\,L^{-1}$ (Sinke *et al.*, 1992), 2.2-24.1 $mg\,L^{-1}$ (Cook & Kelly, 1992), and 9.6-19.2 $mg\,L^{-1}$ (Roberts, 2015).

The German lakes and rivers considered in the present case (Fig. 4.5) have SO_4^{2-} concentrations between 42.6 $mg\,L^{-1}$ in Lake Groß-Glienicke and 167 $mg\,L^{-1}$ in Lake Großer Müggelsee, and are representative within a span of SO_4^{2-} concentration of glacial lakes in Germany with 2.9-340 $mg\,L^{-1}$ (mean 61.6 $mg\,L^{-1}$, 321 lakes) (reviewed by Kleeberg (2012)). In lakes with a SO_4^{2-} concentration below 96-192 $mg\,L^{-1}$, the bacterial sulphate reduction rate is considered to be typically first order, and an increase in SO_4^{2-} concentration will cause an increase in the bacterial sulphate reduction rate (for example Cook & Kelly, 1992).

Usually, it is the rate of SO_4^{2-} supplied to the benthic zone of SO_4^{2-} reduction, which limits bacterial sulphate reduction. An exception are mining lakes, where SO_4^{2-} is scavenged from the water column by Fe hydroxide particles, enhancing the rate of SO_4^{2-} supply to the reduction zone, and increasing bacterial sulphate reduction (for example Rose *et al.*, 1997). Some lakes have extremely high concentrations of SO_4^{2-} with 200-900 $mg\,L^{-1}$, and Fe with 25-620 $mg\,L^{-1}$ (Kleeberg, 1998), but usually these lakes have a low productivity (Nixdorf *et al.*, 2003), and a low supply of organic matter to the sediment. Thus, it remains open, whether the S:Fe ratio can be unrestrictedly applied as an indicator for the presence of vivianite in these extreme environments.

Nonetheless, eutrophic mining lake Golpa IV, Mid-Germany, which was flooded already in 1955, and is today neutral with a pH of 8.35, and a SO_4^{2-} concentration of 234 $mg\,L^{-1}$ (Hupfer *et al.*, 1998), seems to fit in the S:Fe

concept: a high Fe availability leads to a high P retention (compare with Fig. 4.5). In the upper 15 cm of sediment (n = 9 horizons) Fe averaged to 95.5 ± 20.3 mg gdw^{-1}, P to 12.6 ± 8.4 mg gdw^{-1}, and S to 54.3 ± 4.0 mg gdw^{-1}, which resulted in a molar Fe:P ratio of 6.2, and a molar S:Fe ratio of 1.0. According to Fig. 4.5, the latter indicates the presence of vivianite. A direct proof by means of X-ray diffractometry and IR spectroscopy, however, failed at that time, because of the interference with clay minerals (Hupfer *et al.*, 1998).

Given the close coupling of the Fe-, S-, and P-cycles, any (anthropogenically induced) change in the availability of S and Fe may affect vivianite formation, and hence the P budget. The use of $FeSO_4$ in wastewater treatment plants, as a measure to eliminate orthophosphate from wastewater, may limit vivianite formation in the effluent water through increased inputs of SO_4^{2-}. On a larger scale, lignite mining could significantly alter P retention down-stream of former mining areas. While large amounts of Fe oxides readily precipitate, the solubilised SO_4^{2-} is transported further down-stream. This spatially separated supply of Fe and SO_4^{2-} may improve long-term P retention in one location via vivianite authigenesis, but stimulate SO_4^{2-}-induced orthophosphate mobilization in another location (Zak *et al.*, 2006), leading to a loss of Fe-associated binding capacity through enhanced sulfidization of sediments.

Fe additions could be used as a lake restoration, decreasing the orthophosphate concentration in the water by stimulating vivianite formation in the sediment. Through a Fe addition, vivianite formation is favoured, because relatively less Fe is bound in sulphidic form, thus, increasing the P binding capacity of the sediment in the long-term.

4.8 Promoting vivianite formation as a remediation technique to improve water quality

As a consequence of the anthropogenic eutrophication of freshwaters, the in-lake application of P binding agents for P precipitation and inactivation has become an accepted tool aimed at restoring such lake ecosystems (Cooke

et al., 2005; Zamparas & Zacharias, 2014). The most commonly agents are aluminium salts, which inactivate P, thus providing long-term control of P release from sediments. This is, because aluminium salts stably bind orthophosphate regardless of the prevailing redox conditions. Iron is the key element controlling the P binding in aquatic systems because Fe is much more abundant than aluminium in natural systems, and Fe (oxyhydr)oxides are efficient sorption agents for P (Gunnars *et al.*, 2002). Thus, significant amounts of P can be removed from the water body using Fe salts. However, the redox sensitivity of Fe has been regarded as a major disadvantage preventing a long-lasting effect on P mobility (reviewed by Kleeberg *et al.* (2013)). Iron salts such as $FeCl_3$ and $Fe(OH)_3$ are not as frequently used in lake restoration as aluminium salts, and many applications have not been successful (Cooke *et al.*, 2005).

Redox-sensitive Fe-P compounds may be liberated once they encounter anoxic conditions, and thus orthophosphate can be released into the water column. However, this process may be modified by the formation of reduced Fe phosphates. Using a conceptual model, Gächter & Müller (2003) emphasized that an increasing ratio of reactive Fe(II) to reactive P leads to enhanced P burial through the formation of solid ferrous Fe phosphates such as vivianite. The more Fe that is available, the less is captured in sulphidic form. Thus, an increased Fe inventory positively affects the P binding capacity of a sediment. There is field evidence for these theoretical considerations: Kleeberg *et al.* (2012) showed that a single addition of Fe salts to dimictic Lake Groß-Glienicke, Germany, had a beneficial effect on the long-term P cycling in the lake: phosphorus was removed from the water column and chlorophyll-a concentration significantly dropped after the in-lake application of Fe.

Rothe *et al.* (2014) provided evidence that the Fe application in Lake Groß-Glienicke was the stimulus for vivianite formation in the newly forming sediments. Iron was added in surplus in such a way that not all reactive Fe^{2+} precipitated as solid FeS_x. After the Fe addition, total sedimentary P content doubled, and vivianite accounted for approximately 40 % of the increase in sedimentary P. The redox-sensitivity of Fe appeared to be beneficial for the enhanced immobilisation of P. The remaining reactive Fe (not immobilised by the reaction with S^{2-} or bound in vivianite), could migrate upwards with

the newly forming sediment due to its continuous reductive dissolution and re-precipitation. The high mobility of Fe led to increased binding of P and vivianite formation even more than 20 yr after the in-lake measure. Kleeberg *et al.* (2012) emphasized that a lasting effect in terms of P removal and improved water quality can only be maintained, if Fe is provided in surplus. According to Kleeberg *et al.* (2012), the following aspects need to be considered: (1) external "excess" P input, (2) all in-lake P mobilising and Fe removing processes by assuming at least a stoichiometric Fe:P ratio of $\geq$ 2 (Gunnars *et al.*, 2002), (3) the proportion of Fe associated with organic matter, and (4) the proportion of Fe bound by S^{2-}. However, for the in-lake application of any remediation approach, ultimately only a reduction of the external P load can guarantee a beneficial long-term effect on water quality.

Vivianite formation could also be stimulated in constructed wetland systems. In these engineered systems aiming to assist in treating wastewater (Vymazal, 2007), Fe amendments could improve the immobilization of P in the long-term, and especially under anoxic conditions by increasing the P retention capacity of the sediment through vivianite authigenesis.

4.9 Summary and perspectives

Although vivianite is common and the site-specific conditions for its formation are well documented, there is insufficient investigation of both the quantitative importance of vivianite authigenesis for the aquatic P cycle, as well as the mechanisms of its nucleation and crystal growth. Our review shows that vivianite preferentially forms under iron-rich, non-sulfidic conditions, in close proximity to organic remains, not only in freshwaters but also in the marine realm. Vivianite contributes to increased P sequestration in these systems, although data regarding the quantitative contribution of vivianite to P sequestration are generally sparse. An increased P retention through vivianite authigenesis eases eutrophication. However, when a certain organic matter loading is exceeded (S:Fe $>$ 1.5), increased sediment sulfidization leads to reduced or no vivianite formation, and to a corresponding feedback on water column orthophosphate levels. Vivianite formation is affected by

the reductive dissolution of Fe (oxyhydr)oxides and associated orthophosphate release, as well as the production of sulphides and the formation of iron sulphides. However, it is difficult to further specify the processes leading to mineral nucleation and crystal growth in this complex reaction matrix. Based upon findings from microbial batch culture experiments, vivianite nucleation in natural environments eventually appears in nano- to micrometre sized microenvironments which are sustained by microbial activity. Bacteria can locally induce mineral precipitation by modifying the environment surrounding their cells. This small-scale heterogeneity can explain both the occurrence of an assemblage of secondary minerals in close proximity to each other, and the discrepancies arising from thermodynamic equilibrium calculations aimed at predicting vivianite occurrence in sediments.

Significant progress has been recently made in the detection of vivianite due to the application of heavy-liquid separation, which allows analysis of sediment samples naturally enriched in this mineral. The novel approach allows a renewed search for vivianite in surface sediments where it has previously not been detected, in order to identify factors and processes governing the minerals occurrence, and to assess the quantitative importance of vivianite authigenesis in the aquatic P cycle.

The contribution of vivianite to P burial has not yet been sufficiently quantified. Based on the available data, it is difficult to evaluate the long-term effects on water quality of additional P binding through vivianite formation. New reliable methods need to be established and applied to render new insight. More extensive data is needed on prevailing environmental conditions so that we can better understand the causal relationship between nutrient supply, geochemical conditions within the sediment, and the sediment feedback mechanism in finally retaining more or less P as vivianite. The proposed S:Fe ratio as a certain “threshold” may help in selection of additional waters for case studies.

Phosphorus and nitrogen have been recognized as important elements accelerating eutrophication. In addition to these important nutrients, in future studies the role of SO_4^{2-} needs more attention. A simultaneously increasing SO_4^{2-} supply contributes to an immobilization of Fe through the formation

of FeS_x counteracting remediation efforts. Because seawater is much higher in dissolved SO_4^{2-} than is freshwater, the role of vivianite has so far been overlooked in marine waters. However, in coastal surface sediments with high organic matter supply, vivianite formation is induced by a consortium of methane oxidising / sulphate reducing microorganisms, leading to a sink switch from Fe (oxyhydr)oxide-bound P to vivianite. In general, the role of microorganisms in vivianite formation is still not clear. Detailed studies are needed on the contribution of microorganisms on mineral nucleation and crystal growth in sediments. In a first step, using agents selectively inhibiting certain physiological groups of microorganisms might help to identify those groups which are closely associated with the occurrence of vivianite in situ. Only with good understanding of the mechanisms underlying mineral nucleation and the processes leading to the formation of vivianite, models can be developed helping to assess vivianite's significance in the global P cycle.

Chapter 5

Synthesis

In the preceding chapters detailed sediment analyses have been presented, and revealed that the reduced Fe phosphate mineral vivianite ($Fe_3(PO_4)_2 \cdot 8\,H_2O$) is a common P phase in surface freshwater sediments. The conducted studies examplify that vivianite authigenesis can significantly contribute to the binding of P during the initial phase of matter transformation in surface sediments. Notably, the investigations revealed that the sedimentary molar sulphur to reactive Fe ratio (S:Fe) is a valuable indicator for the conditions that affect the formation of the mineral.

To render these findings possible, a novel analytical approach has been developed and applied, allowing the direct identification of vivianite by X-ray powder diffraction (XRD). Initially, the advancement of the methodology has been considered a key factor, because the exploration of vivianite in aquatic sediments requires nothing less than its direct proof within a sediment matrix.

5.1 Summary and discussion

Deep blue inorganic nodules were observed within freeze-dried sediment samples, using a reflected-light microscope, which suggested the presence of vivianite in these samples. The direct identification of vivianite by XRD was finally achieved after application of a heavy-liquid separation of sediment, using different concentrations of a sodium polytungstate solution ($3\,Na_2WO_4 \cdot 9WO_3 \cdot H_2O$). The enrichment of vivianite nodules in high-density samples ($\rho > 2.3\,g\,cm^{-3}$), appearing as deep blue sediment concretions, was

key to demonstrating the presence of vivianite by XRD.

Vivianite identification by XRD has been rendered difficult by some authors, because of its high sensitivity towards oxidation (Bricker III & Troup, 1973; Olsson *et al.*, 1997; März *et al.*, 2008). The present study revealed that vivianite does not loose its diffraction characteristics upon exposure to air, and crystal aggregates were surface oxidised only. The successful detection of vivianite by XRD depends on the amount of vivianite present in the sample, the size and crystallinity of nodules, and the density of X-ray reflexes from other minerals, interfering with those of vivianite.

Based upon the present study, about 5 weight % of vivianite were necessary to identify the mineral, including the three most intensive vivianite peaks clearly visible in the X-ray diffractogram. However, stored above room-temperature, vivianite further oxidises, and alters to an X-ray amorphous phase (for example lipscombite ($Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$), santabarbaraite ($Fe_3^{3+}(PO_4)_2(OH)_3{\cdot}5\,H_2O$), or strengite ($FePO_4{\cdot}2\,H_2O$) (Nriagu, 1972; Nriagu & Dell, 1974; Pratesi *et al.*, 2003)), which appeared yellowish-grey under the reflected-light microscope .

Scanning electron microscopy revealed that vivianite nodules separated from surface sediments of mesothrophic Lake Groß-Glienicke (Berlin, Germany), contained inclusions of diatom shells and other organic debris. These observations indicate that these vivianite nodules were of authigenic origin. The nodules were spherical in shape, had a rough surface texture, and consisted of randomly oriented needle- or plathy-shaped crystals.

Elemental analysis, using scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX), on the surface of particles confirmed that the deep blue nodules mainly consisted of Fe and P (molar Fe:P ratio 1.47), with minor amounts of manganese. The spherical appearance of nodules and their elemental composition was in accordance with findings from others (for example Müller & Förstner, 1973; Rodgers, 1977; Hearn *et al.*, 1983; Frossard *et al.*, 1997; Taylor *et al.*, 2008).

In the present study, vivianite has been detected in the uppermost centimetres of several freshwater sediments such as Lake Groß-Glienicke, Berlin, Germany; Lake Großer Müggelsee, Berlin, Germany; Lake Tegel, Berlin, Ger-

many; Polder Stangenhagen, Brandenburg, Germany, which allows for the conclusion that vivianite is able to form rapidly during early sediment diagenesis. Sapota *et al.* (2006) concluded from the random orientation of crystals, and the rough surface texture of vivianite microconcretions which they detected in sediment cores of Lake Baikal, Siberia, Russia, that sediment pore spaces were not confined by strong compaction, and hence, vivianite must have been formed in an early diagenetic environment in surface sediments.

With a reliable sediment preparation in hand, which allowed a precise determination of the depth distribution of vivianite in a given sediment, the prevailing geochemical conditions revealed important factors and processes, having an influence on vivianite formation. Since vivianite forms from sediment pore solution and crystal growth underlies thermodynamic principles, ultimately, the concentration (activity) of Fe^{2+} and HPO_4^{2-} in solution must exceed the equilibrium value of the mineral, until crystals form. Due to this fact, pore water equilibrium calculations have been a widely used tool, to determine the saturation state of pore water with respect to vivianite, and to predict the occurrence of the mineral in situ. However, those calculations do not necessarily indicate the actual occurrence of a given mineral and may only serve as an indicator for the conditions at which mineral formation is favoured or retarded. Reaction kinetics may ultimately determine mineral nucleation and crystal growth.

The present study revealed discrepancies between supersaturated sediment zones and proven mineral occurrence, indicating that such calculations are not sufficient to predict the occurrence of the mineral in situ. Also other investigators noted the weakness of pore water evidence of vivianite determined from ion activity product calculations (Syers *et al.*, 1973; Cornwell, 1987; Boers & de Bles, 1991), and concluded that the formation of vivianite in sediments is not completely understood (Murphy *et al.*, 2001).

Generally, the validity of pore water equilibrium calculations may be limited due to the following constraints: (i) the calculations are based upon activity coefficients, which are not very accurate, especially for trivalent ions; (ii) there is complexation, in particular in the presence of organic compounds, which increases the solubility and kinetically retards nucleation; and (iii) small

particles (nano-/micrometresized) normally have higher solubilities than bulk particles. Notably, all calculations are based upon macroscopic measurements (using pore water samplers with a theoretical resolution of millimetres to centimetres (Hesslein, 1976)). However, mineral nucleation and crystal growth take place on a nano- to micrometre scale, and might be associated with specific solid phases and the activity of microorganisms. Thus, small-scale in situ conditions within microenvironments are not well represented by such equilibrium calculations (Dodd *et al.*, 2003; Glasauer *et al.*, 2003). Often an assemblage of secondary minerals is found close to each other, indicating that different microenvironmental mineral equilibria must have existed besides each other during mineral formation (Stoops, 1983).

Laboratory batch culture experiments have shown that vivianite forms as a secondary mineral product following Fe reduction by dissimilatory metal reducing bacteria (Fredrickson *et al.*, 1998; Glasauer *et al.*, 2003). The presence of vivianite crystals on the surface of bacterial cell walls (Sánchez-Román *et al.*, 2015) suggests that microorganisms act as nucleation sites for vivianite within sediments, and provide microenvironments where crystal growth is particularly favoured. There are also indications that the particular microorganisms involved in the anaerobic oxidation of methane (AOM) with sulphate and Fe can biomineralise vivianite. Milucka *et al.* (2012) presented evidence for Fe- and phosphate-rich particles appearing within *Desulfosarcina and Desulfococcus* cells in AOM aggregates, which points to the presence of vivianite in these cells. Recently, Egger *et al.* (2015) provided evidence for vivianite authigenesis below a shallow sulphate/methane transition zone, suggesting that the anaerobic oxidation of methane with Fe, facilitated through a consortium of microorganisms, drives a sink-switching from Fe oxide-bound P to vivianite.

Vivianite has been detected in a varity of environments worldwide, including sediments of lakes, rivers, canals, peat bogs, swamps, river fans and marine settings (Nriagu & Dell, 1974; Rodgers, 1977; Nembrini *et al.*, 1983; Cornwell, 1987; Manning *et al.*, 1991; Fagel *et al.*, 2005; Taylor & Boult, 2007; Nanzyo *et al.*, 2010; Cosmidis *et al.*, 2014; Egger *et al.*, 2015). The conditions at which vivianite was detected, has typified its environment. Vivianite occurs

in reducing sediments that are organic- and Fe-rich but non-sulphidic, i.e., where free sulphides (S^{2-}, HS^{-}) readily precipitate to form insoluble metal sulphides, and H_2S is not present.

Indeed, the extent of sulphate reduction relative to the Fe inventory affects the formation of vivianite. The higher the sulphate reduction rate, the more sulphide is produced, and the less Fe remains available, because an increasing portion of Fe is precipitated by the reaction with sulphides. Consequently, pore water Fe^{2+} concentration is too low to promote the formation of vivianite. In the present study, both vivianite and pyrite (FeS_2) have been detected simultaneously in organic-rich sediments. In these sediments redox conditions were low enough to favour the reduction of Fe (oxyhydr)oxides, but H_2S was not present. Notably, vivianite was present at a sedimentary molar sulfur to reactive Fe ratio (S:Fe) smaller than 1.1, only.

The S:Fe ratio is a valuable indicator of the conditions that are important drivers behind the formation or absence of vivianite. More precisely, the molar S:Fe ratio is an indicator of the availability of S relative to that of Fe in the sediment. The higher the S:Fe ratio, the higher the contribution of sulphidic-bound Fe to total Fe. Assuming that the formation of Fe monosulphide is the primary formation product between ferric Fe compounds and H_2S,

$$2\,FeO(OH) + 3\,H_2S \longrightarrow FeS + S^0 + 4H_2O, \text{(Søndergaard } \textit{et al.}\text{, 2002)}$$

a molar S:Fe ratio smaller than 1.5 indicates that there is more reactive Fe available than it could be bound by S^{2-}. By this functional mechanism, the absence and presence of vivianite in different depth layers has been explained for three different freshwater systems, which were investigated in this study.

In lowland river Lower Havel (Berlin, Germany), a decrease in primary production during the last 20 yr caused a decrease in the supply of S to the sediment, and eventually led to the formation of vivianite in the upper 18 cm of the sediment. A lower organic matter supply to sediments, leads to a lower demand for oxidants, resulting in improved redox conditions and lower reduction rates of Fe^{3+} and SO_4^{2-} (Holmer & Storkholm, 2001). Because organic matter is specifically enriched in S compared to Fe (Redfield ratio:

$C_{106}N_{16}P_1S_{0.7}Fe_{0.05}$, (Stumm & Morgan, 1981)), less S^{2-} is produced by desulfuration and dissimilatory sulphate reduction leading to a lower degree of sediment sulfidization (Berner, 1981a), than is produced with a higher organic matter supply. Consequently, the S:Fe ratio decreased with decreasing organic matter production, and vivianite authigenesis was favoured due to a higher availability of Fe^{2+} in pore waters.

In contrast, in Lake Arendsee (Saxony-Anhalt, Germany), an opposite trend was obvious: vivianite was present only in deeper sediment layers but not in the upper 26 cm of the sediment. Here, a massive decline in the Fe content, and an increased supply of organic matter, due to elevated nutrient inputs at the beginning of the 1940's, prevented vivianite authigenesis in surface sediments. In the non-vivianite bearing sediment layers, the ratio of sulphidic-bound Fe on total Fe (degree of sulphidization) was at least 3 times higher compared to the vivianite bearing sediment layers further down-core. Accordingly, the S:Fe ratio was approximately 3 times higher in the non-vivianite bearing sediment layers, compared to the vivianite bearing sediment layers.

In Lake Groß-Glienicke (Berlin, Germany), vivianite formation was triggered by an artificial Fe addition in the year 1992/93, aimed at improving the water quality of the formerly eutrophic lake. Vivianite was present only in sediment layers which were deposited after the in-lake measure, with a sharp transition between vivianite bearing and non-vivianite bearing sediment layers. Due to the Fe addition, the Fe content doubled in the newly forming sediment and the molar S:Fe ratio dropped accordingly. The increased availability of Fe after the restoration measure led to the formation of vivianite, and explained the increased P binding capacity of the sediment. The presented results demonstrate that iron additions can be a sucessfull measure of lake restoration, improving the P retention of the sediment in the long-term (Lewandowski *et al.*, 2013).

In general, in all aquatic systems investigated in this study, vivianite bearing sediment layers were characterised by a higher total P content in comparison to non-vivianite bearing sediment layers. This observation suggests that vivianite significantly contributes to P binding in surface sediments, thus, mitigating eutrophication. However, apart from the common occurrence of the mineral in

freshwater sediments, not much is known about the quantitative importance of vivianite authigenesis in the aquatic P cycle. Recently, the detection of vivianite in Bothnian Sea sediments (Egger *et al.*, 2015) suggests that vivianite significantly contributes to P binding also in coastal marine surface sediments where vivianite authigenesis has so far been disregarded.

Assessing the amount of P bound by vivianite in a particular sediment zone is not trivial, because sequential P extraction procedures, traditionally used to quantify different sedimentary P forms, are not able to selectively solubilize vivianite. Those P extractions differentiate for example between loosly adsobed P, redox-sensitive Fe-bound P, metal-bound P, organic-bound P, Ca-bound P and residual P (Psenner *et al.*, 1984).

In the present study, however, despite of these technical challenges, the amount of vivianite has been assessed for the first time, taking advantage of the enrichment of vivianite nodules achieved after heavy-liquid separation. The amount of vivianite was estimated, combining results from chemical digestion and magnetic hysteresis measurements of vivianite bearing high-density samples.

In case of the chemical digestion approach, the share of vivianite-P to sedimentary TP was calculated, using the dry mass and the P content of the high-density sample, and comparing it with the original sample mass, and the P content prior to heavy-liquid separation. For the magnetic hysteresis approach, the vivianite content in high-density samples ($c_{\text{vivianite}}$ [weight as % of total]) was estimated by comparing the measured paramagnetic mass-specific susceptibility of a high-density sample ($\text{MS}_{\text{sample}}$ [$\text{m}^3\,\text{kg}^{-1}$]) with the tabled value given for vivianite ($\text{MS}_{\text{vivianite}} = 1.05 \times 10^{-6}\,\text{m}^3\,\text{kg}^{-1}$ (Minyuk *et al.*, 2013)). To account for the presence of paramagnetic iron sulphides in high-density samples, the measured mass-specific susceptibility was corrected by the amount iron sulphides present in these samples. Thus, the vivianite content could be calculated according to the following equation:

$$\begin{aligned} c_{\text{vivianite}} &= \frac{(\text{MS}_{\text{sample}} - \text{MS}_{\text{sample, FeS}})}{\text{MS}_{\text{vivianite}}} \times 100 \\ &= \frac{(\text{MS}_{\text{sample}} - (\text{MS}_{\text{FeS}} \times c_{\text{FeS}}))}{\text{MS}_{\text{vivianite}}} \times 100, \end{aligned} \tag{5.1}$$

where $MS_{sample,\ FeS}$ [$m^3\,kg^{-1}$] is the contribution of paramagnetic FeS to the measured mass-specific susceptibility, and c_{FeS} is the content of FeS [weight as % of total] in a high-density sample.

In Lake Groß-Glienicke, vivianite accounted for 20 % of total sedimentary P in surface sediments. Thus, based on the observation that the P content doubled after the in-lake application of Fe, vivianite authigenesis explained 40 % of this increase in P binding capacity in Lake Groß-Glienicke. Similar results were obtained by both the chemical digestion and the magnetic hysteresis approach, confirming the robustness of the estimate. For Lake Arendsee and lowland river Lower Havel, chemical digestion data of high density samples naturally rich in vivianite revealed a contribution of vivianite to total sedimentary P of 46 % and 11 %, respectively.

These findings examplify that vivianite can make up a significant contribution to P retention in surface sediments. However, the results also reveal, that vivianite authigenesis cannot explain the observed increase in sedimentary total P in vivianite bearing sediment layers alone. Due to a general increase of the reactive Fe pool in vivianite bearing sediment layers, Fe (oxyhydr)oxides which resisted reductive dissolution in the anoxic sediment (De Vitre *et al.*, 1988; Hyacinthe & Van Cappellen, 2004) contributed to the elevated P binding capacity in those vivianite bearing sediment zones, too.

5.2 Conclusion and outlook

The present study has demonstrated, that vivianite is a common authigenic mineral phase in surface freshwater sediments, and significantly contributes to P burial. The study has shown that Fe additions can be successfully used to restore eutrophied lakes, leading to an increased P binding capacity of sediments through stimulation of vivianite formation. Investigations including the analysis of pore water, and the separation of sediment by application of a heavy-liquid separation revealed important findings on the factors and processes governing vivianite formation in surface freshwater sediments.

Vivianite occurs in organic-rich sediments under non-sulphidic conditions, and readily forms if the solution concentration of Fe^{2+} and HPO_4^{2-} are above

the critical value at which mineral grains nucleate. The availability of Fe (oxyhydr)oxides, their reductive dissolution, and the associated orthophosphate release, as well as the production of sulphides and the formation of Fe sulphides, play a major role in vivianite formation. Microorganisms directly or indirectly affect vivianite authigenesis by modifying the chemical environment surrounding their cells, thus, locally inducing mineral precipitation. However, the role of microorganisms in vivianite formation is still not clear. It remains open which specific mechanisms lead to crystallization of mineral grains in this complex reaction matrix.

Increased primary production can impede the formation of vivianite, depending on the available pool of Fe not being bound by sulphides, and the supply of orthophosphate in pore waters. When a certain amount of organic matter load is exceeded, increased sediment sulphidization leads to less or no vivianite formation and a respective feedback on water column phosphate levels. Only if the molar S:Fe ratio stays below a value of 1.5, vivianite formation is favoured. Thus, anthropogenically induced eutrophication of freshwaters, and the accompanied increase in organic matter production, may have prevented vivianite formation in recent sediments, which led to a negative feedback in terms of water quality.

Nonetheless, vivianite is not an indicator of nutrient-rich or nutrient-scarce conditions, but rather its occurrence mirrors the extent of Fe oxide availability to that of S^{2-} production under a given supply of organic matter. Thus, depending on the Fe inventory, vivianite formation is favoured under a range of nutrient conditions. The proposed sedimentary S:Fe ratio as a certain "threshold" may help to screen several other sediments for the occurrence of vivianite, thereby confirming a general mechanism that crucially affects vivianite formation in surface sediments.

Despite of the significant progress which has been made in the detection of vivianite in surface sediments, the contribution of vivianite to P retention has not yet been sufficiently quantified. Long-term effects of vivianite authigenesis on water quality through enhanced P binding remain largely unknown. In future studies, new methods need to be established and applied

in order to understand which mechanisms underly mineral nucleation, and which processes lead to crystal growth in sediments. Only with a fundamental understanding of vivianite formation in sediments, the quantitative role of vivianite in the global P cycle can be better assessed.

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Declaration

I hereby declare that this thesis and the work presented in it is entirely my own except where otherwise indicated. I have only used the documented utilities and references.

Hiermit erkläre ich, dass ich die vorliegende Dissertation selbständig verfasst habe und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Berlin, 29th January 2016 .....

Matthias Rothe